

**TAM/WASP TOXICS SCREENING LEVEL MODEL
FOR THE ANACOSTIA RIVER**

-Preliminary Draft Report-

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CHAPTER 1: INTRODUCTION

The Anacostia River runs through the heart of our nation's capitol and drains an urban/suburban watershed that covers a portion of the District of Columbia and its Maryland suburbs. The Anacostia has long suffered from ills common to our nation's urban rivers, including low levels of dissolved oxygen, high sedimentation rates, high bacteria counts, and problems arising from the presence of toxic chemicals. Toxic chemicals including polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), metals, and pesticides such as chlordane and DDT have been detected in the river's bed sediments (LTI, 1989?; Velinsky et al., 1992; Velinsky et al., 1994; Velinsky et al., 1997; Velinsky and Ashley, 2001; Wade et al., 1994). Fish consumption advisories have been in place since 1987 due to unacceptable levels of PCB and chlordane in certain Anacostia fish. PAHs are suspected to be the cause of the high rate of tumors in brown bullheads in the Anacostia reported by the U.S. Fish and Wildlife Service (Pinkney, 2000). A preliminary risk assessment for the Anacostia Watershed Toxics Alliance (AWTA) found that a variety of species of aquatic life, birds, and mammals were potentially at risk due to the presence of toxic chemicals in the river (Syracuse Research Corporation, 2000). Because of problems related to toxic chemicals, the Anacostia was designated a "Region of Concern" by the Chesapeake Bay Program in 1993.

The District of Columbia Department of Health (DC DOH) has developed the *Anacostia River Toxics Management Action Plan* (DC Environmental Regulation Administration, 1996) to serve as a guide for addressing the problem of toxic chemicals in the river. The Anacostia has been placed on the District's 303(d) list of impaired waterbodies, and the District is currently in the process of determining Total Maximum Daily Load (TMDL) allocations for toxic chemicals that will allow the Anacostia to meet water quality standards. To assist in the TMDL allocation process, DC DOH has asked the Interstate Commission on the Potomac River Basin (ICPRB) to construct a computer model capable of simulating the daily concentrations of toxic chemicals in the District's portion of the Anacostia River, and of predicting the changes in these concentrations under potential load reduction scenarios.

1.1. Background

The Anacostia River watershed encompasses an area of approximately 176 square miles in the District of Columbia and Maryland. The watershed lies within two physiographic provinces, the Piedmont Plateau and the Coastal Plain, whose division runs approximately along the Montgomery/Prince Georges County line. The upper northwestern portion of the watershed lies within the Piedmont Plateau province, characterized by steep stream valleys and well-drained loamy soils underlain by metamorphic rock. The remainder of the basin lies within the Coastal Plain province, a wedge-shaped mass of primarily unconsolidated sediments drained by slowly meandering streams. The location of the watershed and its three major drainage areas, the Northeast Branch, the Northwest Branch and the tidal drainage areas, are depicted in Figure 1-1. The drainage areas of the Northwest and Northeast Branches, 53 mi² and 76 mi², respectively, comprise approximately 73% of the total area of the watershed. The Anacostia River begins in

Bladensburg, Maryland, at the confluence of its two major tributaries, the Northwest Branch and the Northeast Branch, and flows a distance of approximately 8.4 miles before it discharges into the Potomac River in Washington, DC. Because of its location in the Washington metropolitan area, the majority of the watershed is highly urbanized, with a population of 804,500 in 1990 and a projected population of 838,100 by the year 2010 (Warner et al., 1997). An analysis of GIS layers prepared by the Metropolitan Washington Council of Governments (MWCOC), indicates that land use in the watershed is approximately 43% residential, 11% industrial/commercial, and 27% forest or wetlands, with 22.5% of the area of the watershed covered by impervious surfaces (see Shepp et al., 2000).

The Anacostia River is actually an estuary, with tidal influence extending some distance into the Northeast and the Northwest Branches, approximately to the USGS gage stations 01649500 at Riverdale Road, and 0165100 at Queens Chapel Road (see Figure 1-1). However, water in the tidal portion of the river is fresh water, with negligible values of salinity. The variation in the river's water surface elevation over a tidal cycle is approximately 3 feet. From an analysis by the National Oceanographic and Atmospheric Administration (NOAA) of sounding data taken by the US Army Corps of Engineers prior to a 1999 dredging project combined with additional bathymetry data taken by the Navy in the summer of 2000, the volume of the tidal portion of the river at mean tide is approximately 10,000,000 cubic meters (m^3), with a surface area of approximately 3,300,000 square meters (m^2). The width of the river varies from approximately 60 meters (m) in some upstream reaches to approximately 500 m near the confluence with the Potomac, and average depths across the channel transects vary from approximately 1.2 m upstream of Bladensburg to about 5.6 m just downstream of the South Capital Street Bridge. The average daily combined discharge of the Northeast and Northwest Branches into the tidal river is approximately 370,000 m^3 . During non-storm conditions, measured flow velocities during the tidal cycle have been in the range of 0 to 0.3 m/sec (Katz et al., 2000; Schultz and Velinsky, 2001).

1.2. TAM/WASP Modeling Framework

The TAM/WASP Toxics Screening Level Model simulates the loading, fate, and transport of toxic chemical contaminants in the tidal portion of the Anacostia River, and can predict the changes over time of concentrations of these contaminants in both the river's water and in the surficial bed sediment. The toxics model is based on ICPRB's TAM/WASP modeling framework, which was first used to construct a eutrophication/sediment oxygen demand model for the District's dissolved oxygen TMDL (Mandel and Schultz, 2000). The sediment transport capabilities of the model were then further developed, resulting in TAM/WASP Version 2.1 (Schultz, 2001), which was used by the District to develop its suspended solids TMDL. The TAM/WASP Toxics Screening Level Model, TAM/WASP Version 2.2, uses, with only minor changes, the hydrodynamic model and the sediment transport model components of Version 2.1.

The TAM/WASP Toxics Screening Level Model includes three primary components:

1. A hydrodynamic component, based on the Tidal Anacostia Model (TAM), originally

- developed at MWCOG in the 1980's (Sullivan and Brown, 1988). This component simulates the changes in water level and water flow velocities throughout the river due to the influence of tides and due to the various flow inputs entering the river. The original 15 segment hydrodynamic model has been upgraded by ICPRB to a 36 segment model with side embayments (Schultz, 2003).
2. A load estimation component, constructed by ICPRB using Microsoft ACCESS. Water containing sediment and chemicals flows into the river every day from a variety of sources, including the upstream tributaries (the NE and NW Branches), the tidal basin tributaries (Lower Beaverdam Creek, Watts Branch and others), the combined sewer system overflows (CSOs), the DC separate storm sewer system, and ground water. The ICPRB load estimation component estimates daily water flows into the river based on USGS gage data for the NW and NE Branches and National Airport daily precipitation data for flows from other sources. It also estimates daily sediment and chemical loads into the river.
 3. A water quality component, based on the EPA's Water Quality Analysis Simulation Program (WASP-TOXI5) for sediments and toxic contaminants (Ambrose et al., 1993). This component simulates the physical and chemical processes that transport and transform chemical contaminants that have entered the river. The WASP sediment/toxics transport module has been enhanced by ICPRB to more realistically simulate sediment erosion and deposition processes based on hydrodynamic conditions (see Schultz, 2001).

TAM/WASP is a one-dimensional (1-D) model, that is, it simulates processes in the river by idealizing the river as a long channel where conditions may vary along the length of the channel but where conditions are assumed to be uniform throughout any channel transect (i.e. from left bank to right bank). Approximating the river as a one-dimensional system is reasonable given the results of the summer 2000 SPAWAR study, which concluded that throughout a channel transect, the water in the river was generally well-mixed, and current velocities were relatively homogenous and primarily directed along the axis of the channel (Katz et al., 2001). It is also supported by model simulations carried out subsequent to a dye study conducted in 2000 by LimnoTech, Inc. (LTI) (LTI, 2000). These results showed that a 35 segment 1-D model was capable of simulating fairly well the time evolution of dye concentrations in the tidal river (DC WASA, 2001; Schultz, 2003)

In ICPRB's TAM/WASP Version 2, the main channel is divided along its length into 35 model segments, extending from the Bladensburg Road bridge in Prince Georges County, MD, to the Anacostia's confluence with the Potomac in Washington, DC (see Figure 1-2). Additionally, WASP model segment 36, representing Kingman Lake, adjoins segment 19. (Kingman Lake is represented as a tidal embayment to segment 19 in the TAM hydrodynamic model.) Each of the 36 water column segments is underlain by a sediment segment, as shown schematically in Figure 1-3. Sediment segment 72 underlies the water column segment 36, representing Kingman Lake, not represented in Figure 1-3.

1.3. Sediment Transport Model Component

The WASP model allows the simulation of the fate and transport of up to three sediment grain size fractions. In TAM/WASP Version 2, the three sediment size fractions modeled are:

<u>Frac1</u> : coarse-grained sediments:	> 120 μm	(fine sands to gravel)
<u>Frac2</u> : medium-grained sediments:	> 30 μm and < 120 μm	(fine silts to very fine sands)
<u>Frac3</u> : fine-grained sediments	< 30 μm	(clays and very fine silts)

In TAM/WASP Version 1, a new capability was added to WASP-TOXI5 by ICPRB to allow simulation of sediment transport based on model hydrodynamics (Mandel and Schultz, 2000). This capability has undergone further development in TAM/WASP Version 2, in order to support the use of the model for the prediction of fate and transport of toxic chemicals. The fine-grained and medium-grained sediment fractions are treated in TAM/WASP as cohesive sediments, and the algorithms governing their transport follow the approach developed by Partheniades (1962) and Krone (1962), which has frequently been employed in other models, such as the Hydrologic Simulation Program FORTRAN, (HSPF) model (Bicknell et al. 1993) and the Army Corps of Engineer's HEC-6.

For the two cohesive sediment fractions, erosion and deposition are a function of bed shear stress. Erosion occurs when shear stress exceeds a critical shear stress and is proportional to the extent it exceeds the critical shear stress. Similarly, the deposition of cohesive sediment occurs when shear stress is less than a critical threshold--distinct from the critical shear stress for erosion--and occurs in proportion to the drop in shear stress below the threshold. Bed shear stress is calculated from the slope of the energy grade line, which is determined by solving Manning's equation, resulting in a relationship between bed shear stress and flow velocity. Distinct values of the zero-flow settling velocity, the erosion velocity multiplier, critical shear stress, and the critical deposition threshold are entered by the user for fine-grained and medium-grained sediment fractions.

To model the transport of the coarse-grained sediment fraction, a simple power law method is used. The transport of the coarse-grained sediment fraction (i.e. sand and gravel) is modeled by determining the carrying capacity of the flow, which in turn is dependent on the flow's hydrodynamic properties. If flow conditions change so that the carrying capacity exceeds the concentration of sand currently being transported, additional sand will be eroded from the bed. If the concentration of sand exceeds its carrying capacity, sand will be deposited.

The TAM/WASP sediment transport model, in addition to predicting water column concentrations of total suspended solids (TSS) that are in reasonably good agreement with available data, does a good job of predicting the spatial pattern of bed sediment grain size distribution., including the high proportion of coarse-grained sediment found near the mouths of

the upstream tributaries and Watts Branch and the high proportion of fine-grained sediment found in the downstream portion of the tidal river. Details concerning the performance of the TAM/WASP Version 2 sediment transport component are given in ICPRB's report on the calibration of the sediment transport model (Schultz, 2001).

1.4. Data Support

This modeling effort relies upon a number of data sets to compute model inputs and to provide data for model calibration and verification. The data sets used to support the hydrodynamic and sediment transport components of the model were discussed in the report on the sediment transport model calibration (Schultz, 2001). The primary data sets used to support the toxic chemical fate and transport component of the model are described in the sections below.

1.4.1. Storm and non-storm monitoring data

Storm and non-storm monitoring data are used to compute daily stormflow and baseflow load inputs for the model. The following three data sets were those primarily used for load calculations:

Upstream tributary study by Gruessner et al. (1998) ICPRB conducted a study for DC DOH on toxic chemical concentrations in the upstream tributaries to the Anacostia, the Northeast and Northwest Branches. For this study, water samples were collected from both tributaries in 1995-96 during four storm events and six non-storm events and concentration values were reported for all chemicals modeled except arsenic. Chemical analyses were performed at detection limits low enough to quantify loads. Sample collection locations were at the US Geological Survey's Northeast Branch and Northwest Branch gage stations, Stations 01649500 and 0165100, shown in Figure 1-1.

District of Columbia MS4 monitoring data (Nicoline Shelterbrandt, private communication, 2002) The Water Quality Division of the DC DOH is conducting Municipal Separate Storm Sewer System (MS4) monitoring at a number of locations as part of the requirements for the District's National Pollutant Discharge Elimination System (NPDES) permit (MS4 NPDES Permit No.DC0000221, First Annual Review, Volume III). For this modeling effort, ICPRB had available MS4 monitoring data collected from June 1, 2001 through June 13, 2002 at the following locations in the Anacostia tidal basin: Stickfoot sewer, O St. pumping station (separate sewer line), Gallatin at 14 St., Varnum and 19th Place (later Varnum and 22nd Place), Nash Run, Hickey Run at V St. and 33rd St., Oklahoma and D St., and East Capitol Street (west). In this study, for some of the chemicals modeled, analyses have been performed at detection limits low enough to quantify loads.

Prince Georges County Monitoring Data (Dr. Mou Soung Cheng, private communication, 2001) Prince Georges (PG) County collects samples from Lower Beaverdam Creek and Watts Branch at locations in PG County as part of its storm water monitoring program, and these samples are analyzed for a variety of chemicals including zinc, lead, and copper and other metals. For this

modeling effort, ICPRB had available data from the years 1994-99.

DC Water and Sewer Authority Long Term Control Plan Monitoring The DC Water and Sewer Authority conducted monitoring of storm water discharges from CSOs as well as some tributaries and SS locations, in 1999 and 2000 in support of its development of its Long Term Control Plan to address the CSO problem (DC WASA, 2000a; 2000b; 2000c). Though the primary aim of the monitoring study was to better understand loads of constituents contributing to the dissolved oxygen problem in the river, some analyses were also done for toxic contaminants. Though detection limits used for analyses for organic chemicals were not low enough to provide data to quantify loads, useful data was obtained for metals.

1.4.2. Main channel water column data

Data on water column concentrations of chemicals in the main channel of the Anacostia make possible a comparison of model predictions with empirical observations, and are used in the model calibration and verification process. Data from the following studies was used in the calibration/verification of the TAM/WASP Toxics Screening Level Model:

Study on the effects of stormwater runoff (Velinsky et al., 1999) In this study, water samples were collected in 1998 at seven stations in the main channel of the Anacostia, as well as at three additional locations: in the Potomac River near the confluence with the Anacostia, and at the Northeast and Northwest Branches. Samples were collected on four days prior to storm events, and on five days subsequent to storm events. Data is available for some of the chemicals included in the model, and with detection limits low enough to be suitable for comparison with model predictions.

Study on the fate and transport of sorbed PAHs (Coffin et al. 1998) In this study, water samples were collected at four stations in the main channel of the Anacostia during 3 sampling events (Nov 1997, Feb 1998, and May 1998). Water samples were analyzed for concentrations of sorbed PAHs only (i.e. total and dissolved constituents not reported).

Study on the distribution of PAHs along the tidal Anacostia (Katz et al. 2000) In this study, water samples were collected at 14 stations in the main channel of the Anacostia during a 1-day sampling period (July 12, 2000). Water samples were analyzed for concentrations of total PAHs, as well as other constituents.

1.4.3. Bed sediment chemical concentration data

Data on toxic chemical concentrations in the river's bed sediment is used, with the help of Geographic Information System (GIS) software, to characterize the spatial pattern of chemical contaminants in the river bed (see Section 3.2.1). These empirical results are then compared with model predictions of bed sediment contaminant concentrations as part of the model calibration and verification process. The most comprehensive bed sediment concentration data set was collected by Velinsky and Ashley in 2000. In addition, several smaller historical (post-

1994) data sets were used to provide information on contaminant concentrations in areas immediately adjacent to facilities that are thought to be potential sources of certain contaminants. Figure 1-4 shows the sediment sampling locations for the studies listed below:

Study of chemical contaminants in Anacostia River bed sediments (Velinsky and Ashley, 2002)

In September of 2000, in a study sponsored by the DC DOH and the AWTa, bed sediment samples were collected from 128 locations within the main channel of the Anacostia or nearby areas in the Potomac. Samples were analyzed for a wide variety of chemical contaminants, including all of the constituents considered in this modeling effort.

AWTA/NOAA Database NOAA has constructed a database for the Anacostia Watershed Toxics Alliance containing a number of historical data sets with bed sediment contamination data (NOAA, 2001). Many of these data sets are a result of site investigations conducted by individual facilities located adjacent to the river. For the calibration of the TAM/WASP Toxics Screening Level Model, the post-1994 data sets from this database were combined with the data collected by Velinsky and Ashley to provide a picture of sediment contamination in the Anacostia. Table 1-1, below, contains a summary of the relevant studies extracted from this database as well as the number of stations for each chemical.

Table 1-1. Number of Surficial Sediment Sampling Stations per Chemical from AWT/NOAA Database

Study ¹	Zinc	Lead	Copper	Arsenic	PCB	PAH	Chlordane	Hepta Epox	Dieldrin	DDT
1995 PEPCO	5	5	x	x	5	x	6	4	5	5
1995 Washington Navy Yard	7	7	7	7	1	40	x	x	x	7
1996 FWS PAH/PCB - Mason Neck	x	x	x	x	x	x	x	x	x	2
1996 WA Gas - East Station Project	8	8	8	7	x	7	x	x	x	x
1996 Wetland Restoration - Kenilworth	2	2	2	2	x	x	2	2	x	x
1997 DC Sed Core Analysis	6	6	6		6	x	6	1	6	6
1998 USACE Federal Navy Channel	4	4	4	4	x	x	x	x	x	4
1999 WA Navy Yard RI	32	32	32	30	x	x	x	x	x	x
2000 Velinsky AR Sed ²	128	128	128	x	126	125	122	122	119	120
Total # of Stations	192	192	187	50	138	172	136	129	130	144

¹ All data from studies extracted from AWT/NOAA database (NOAA, 2001) with the exception of 2000 Velinsky AR Sed.

² Source: Velinsky and Ashley (2001).

1.5. Model Constituents

The TAM/WASP Toxics Screening Level Model uses WASP-TOXI5 to simulate many of the chemical and physical transformation processes that affect the fate of toxic chemicals in the river. Because WASP-TOXI5 can only simulate three chemicals at a time, a total of seven sub-models have been constructed. Most of the organic chemicals considered are actually classes of related constituents, including isomers and breakdown products. For a given class of chemicals, for example, DDTs, data was not available for all of constituents in the class, and therefore the sub-model only includes those constituents for which there is adequate data support. Also, for some sub-models, constituents are grouped together for convenience because of the three chemical limitation of WASP. In these cases an effort is made to group together constituents with similar physical and chemical properties. The sub-models and the constituents represented in each of them are given in Table 1-2. Tables 1-3 and 1-4 list some of the physical and chemical properties by sub-model grouping of PCB homologs and of individual PAHs, and are meant to provide a rationale for the choice of groupings.

1.5.1. Inorganic chemicals sub-models

Two sub-models have been constructed to simulate the fate and transport of inorganic chemicals in the tidal Anacostia. The first is a sub-model for the following metals (Metals1): zinc, lead, and copper. The second is a sub-model for arsenic (Metals2). Chemical speciation of these four constituents is not simulated due to lack of data support.

1.5.2. PCB sub-model

In the PCB sub-model, PCB congeners are grouped into three classes. The first group, PCB1, consists of homologs 2 and 3, that is, of PCB congeners with 2 or 3 chlorine atoms. The second group, PCB2, consists of homologs 4, 5, and 6, and the third group, PCB3, consists of homologs 7, 8, and 9. It should be noted that in the data sets used in this project, concentrations for typically only roughly one half of the possible 209 PCB congeners were reported. Furthermore, the particular congeners with reported values differed somewhat from data set to data set, leading to some degree of inconsistency for different model components in the computed sums of congeners concentrations for the three PCB groupings. For a list of the PCB congeners with reported values for each of the studies used in this project, see Table A-1 in the Appendix. Because of the differences in reported congeners in different data sets, homolog 1, that is, the set of all PCB congeners with just one chlorine atom, which comprise only a small fraction of the total PCB mass, is not considered in the groupings. Similarly, homolog 10 is not included in any of the groups because the only PCB congener with 10 chlorine atoms, congener 209, is not included in most of the available data sets.

In support of the groupings used in the PCB sub-model, Table 1-3 gives values for the molecular weights (MW), partition coefficients (K_d 's), Henry's Law coefficients (HLCs), and reported aerobic biodegradation potential for homologs 2 to 9. The average partition coefficients listed were computed from 1998 Anacostia River water column data (Velinsky et al., 1999).

1.5.3. PAH sub-model

The PAH sub-model includes the 16 individual PAHs which had reported values in the 1995-96 study on upstream loads (Gruessner et al., 1998). These 16 PAHs were also all included in the 2000 study of bed sediment concentrations by Velinsky and Ashley. The PAH sub-model simulates the fate and transport of three groups of the individual PAHs, as listed in Table 1-4 (also see Table 1-2). The first group, PAH1, is the sum of six 2 and 3-ring PAHs: naphthalene, 2-methyl naphthalene, acenaphthylene, acenaphthene, fluorene, and phenanthrene. The second group, PAH2, consists of four 4-ring PAHs: fluoranthene, pyrene, benz[a]anthracene, and chrysene. The third group, PAH3, consists of six 5 and 6-ring PAHs: benzo[k]fluoranthene, benzo[a]pyrene, perylene, indeno[1,2,3-c,d]pyrene, benzo[g,h,i]perylene, and dibenz[a,h+ac]anthracene.

In support of the groupings used in the PAH sub-model, Table 1-4 gives values for the molecular weights (MW), partition coefficients (K_d 's), and Henry's Law coefficients (HLCs) for the 16 PAHs included in the model. The average partition coefficients listed were computed from 1995-96 Northeast and Northwest Branch water column data (Gruessner et al., 1998).

1.5.4. Pesticides sub-models

Sub-models have been constructed for chlordane, dieldrin, heptachlor epoxide, and DDT. The choice of constituents included in the sub-models is based on data availability. The PEST1 sub-model simulates the fate and transport of heptachlor epoxide and total chlordane, which in this modeling study consists of the sum of three chlordane isomers/metabolites: cis-chlordane, trans-nonachlor, and oxychlordane. The DDT sub-model simulates the fate and transport of three individual DDT isomers/metabolites: p,p DDD, p,p DDE, and p,p DDT. Dieldrin is modeled individually in the PEST2 sub-model.

Table 1-2. Constituents Represented

Constituent	WASP Variable
Metals 1 Model	
zinc	CHEM1
lead	CHEM2
copper	CHEM3
Metals 2 Model	
arsenic	CHEM1
PCB Model	
2 chlorinated homolog	PCB1
3 chlorinated homolog	
4 chlorinated homolog	PCB2
5 chlorinated homolog	
6 chlorinated homolog	
7 chlorinated homolog	PCB3
8 chlorinated homolog	
9 chlorinated homolog	
PAH Model	
napthalene	PAH1 (2 and 3 ring PAHs)
2-methyl napthalene	
acenapthylene	
acenapthene	
fluorene	
phenanthrene	
fluoranthene	PAH2 (4 ring PAHs)
pyrene	
benz[a]anthracene	
chrysene	
benzo[k]fluoranthene	PAH3 (5 and 6 ring PAHs)
benzo[a]pyrene	

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perylene	
indeno[1,2,3-c,d]pyrene	
benzo[g,h,i]perylene	
dibenz[a,h+ac]anthracene	
PEST1 Model	
Chlordane (cis-chlordane + trans-nonachlor + oxychlordane)	CHEM1
Heptachlor epoxide	CHEM2
PEST2 Model	
Dieldrin	CHEM1
DDT Model	
4,4'-DDD	DDD
4,4'-DDE	DDE
4,4'-DDT	DDT

Table 1-3. Rational for PCB Groupings

WASP Variable	PCB Homolog	MW (g/mole)	Mean Baseflow K_d^1 (L_w/kg_s)	Average HLC² (atm – m³/mole)	Aerobic Biodegradation Potential
CHEM1	Dichlorobiphenyl	223.1	19,988	2.34E-04	Rapid
	Trichlorobiphenyl	257.5	52,291	1.88E-04	Rapid
CHEM2	Tetrachlorobiphenyl	292.0	136,823	1.49E-04	Slow
	Pentachlorobiphenyl	326.4	181,487	0.84E-04	Resistant
	Hexachlorobiphenyl	360.9	259,465	0.36E-04	Resistant
CHEM3	Heptachlorobiphenyl	396.3	765,233	0.15E-04	Resistant
	Octachlorobiphenyl	429.8	558,671	0.13E-04	Resistant
	Nonachlorobiphenyl	464.2	Insufficient data	Not reported	Resistant

¹ Mean K_d based on tidal Anacostia baseflow water column data (Velinsky et al., 1999)

² Adapted from Brunner et al., 1990

Table 1-4. Rational for PAH Groupings

WASP Variable	PAH Analyte	MW (g/mole)	Mean Baseflow K_d^{-1} (L _w /kg _s)	Average HLC ² (atm – m ³ /mole)
CHEM1 (2 and 3 ring PAHs)	napthalene	128.2	10775	1.44E-03
	2-methyl napthalene	142.2	35,470	5.18E-04
	acenapthylene	152.2	66,426	5.25E-04
	acenapthene	154.2	17320	1.69E-04
	fluorene	166.2	9,584	6.94E-05
	phenanthrene	178.2	65,194	1.26E-04
CHEM2 (4 ring PAHs)	fluoranthene	202.2	268,884	3.98E-04
	pyrene	202.3	491,870	9.31E-06
	benz[a]anthracene	228.3	678,999	4.35E-06
	chrysene	228.3	695,794	1.88E-06
CHEM3 (5 and 6 ring PAHs)	benzo[k]fluoranthene	252.3	1,517,320	1.35E-05
	benzo[a]pyrene	252.3	2,276,973	4.04E-07
	perylene	252.3	513,160	4.03E-06
	indeno[1,2,3-c,d]pyrene	276.3	1,769,475	6.73E-07
	benzo[g,h,i]perylene	276.3	901,534	2.06E-07
	dibenz[a,h+ac]anthracene	278.4	5,832,155	1.23E-07

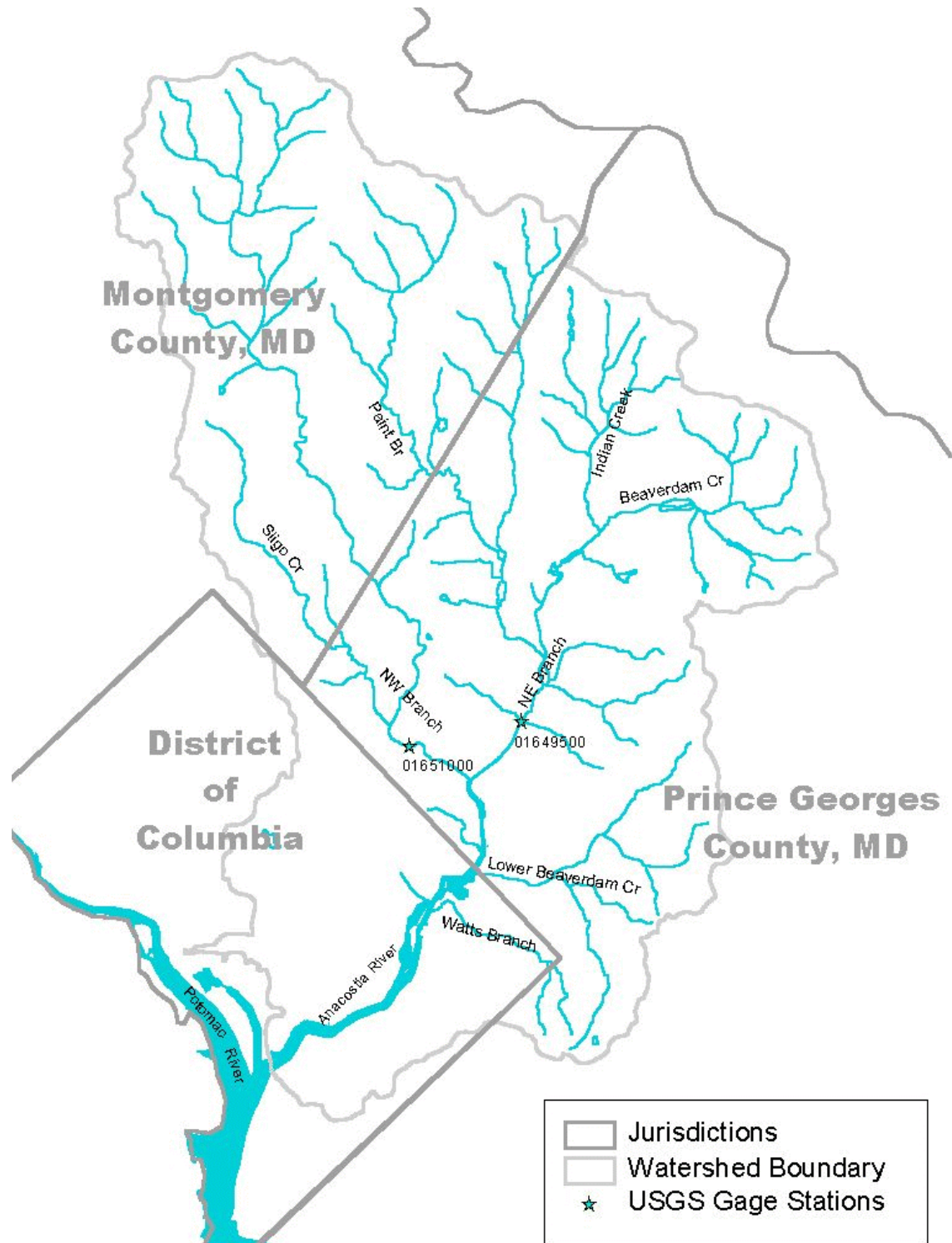


Figure 1-1. Anacostia Watershed

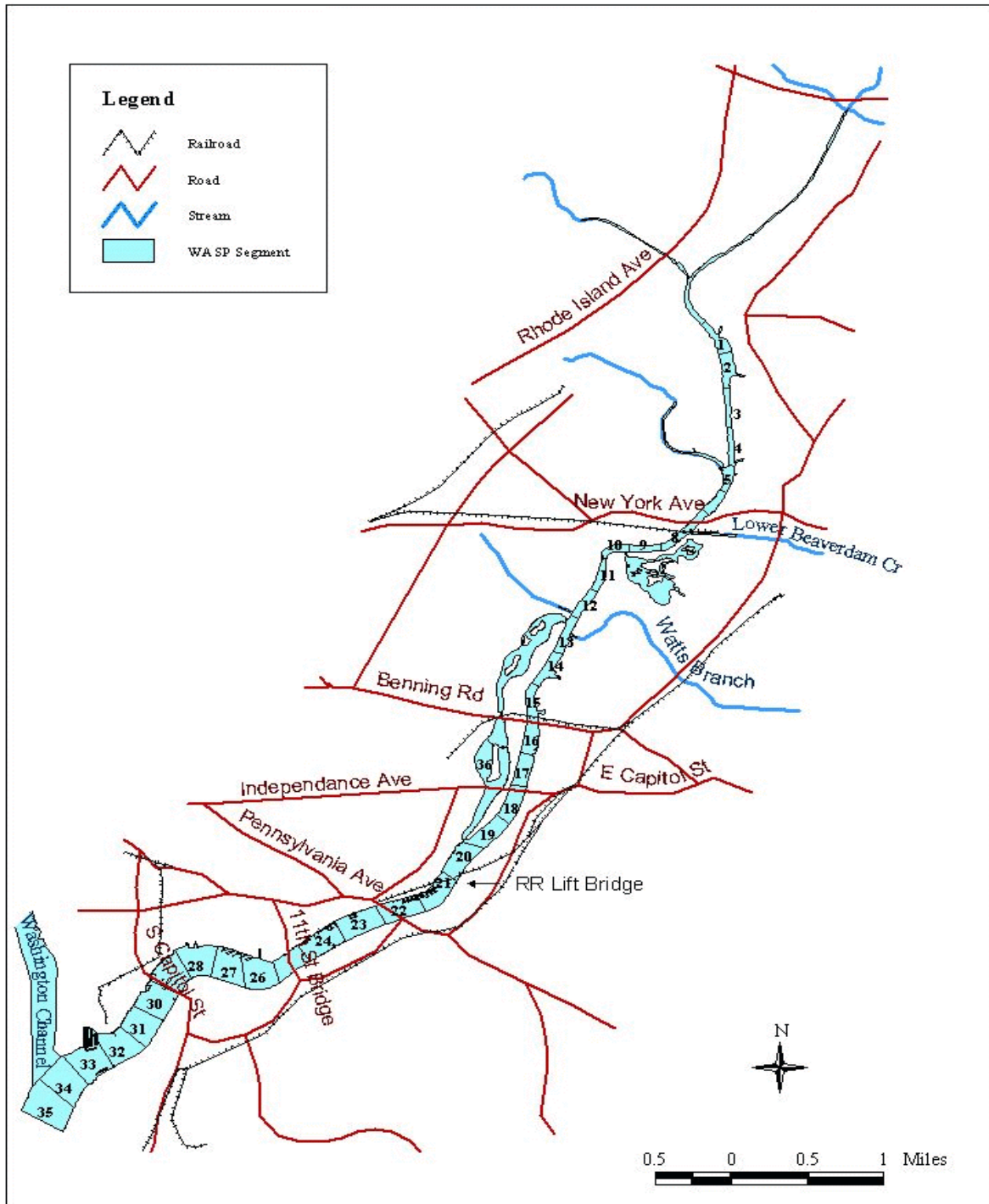


Figure 1-2. TAM/WASP Version 2 Model Segmentation

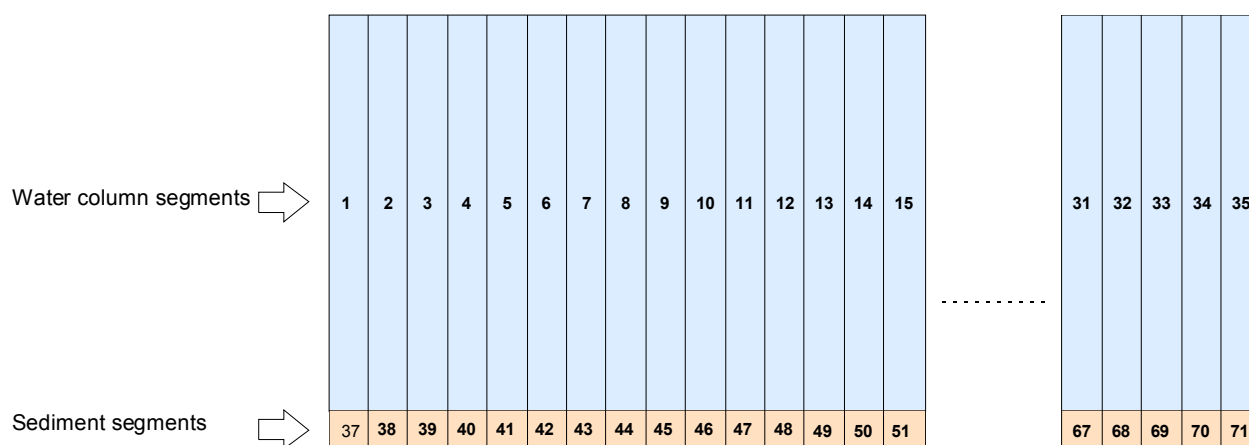


Figure 1-3. Schematic Representation of Location of Sediment Segment Underlying Water Column Segments

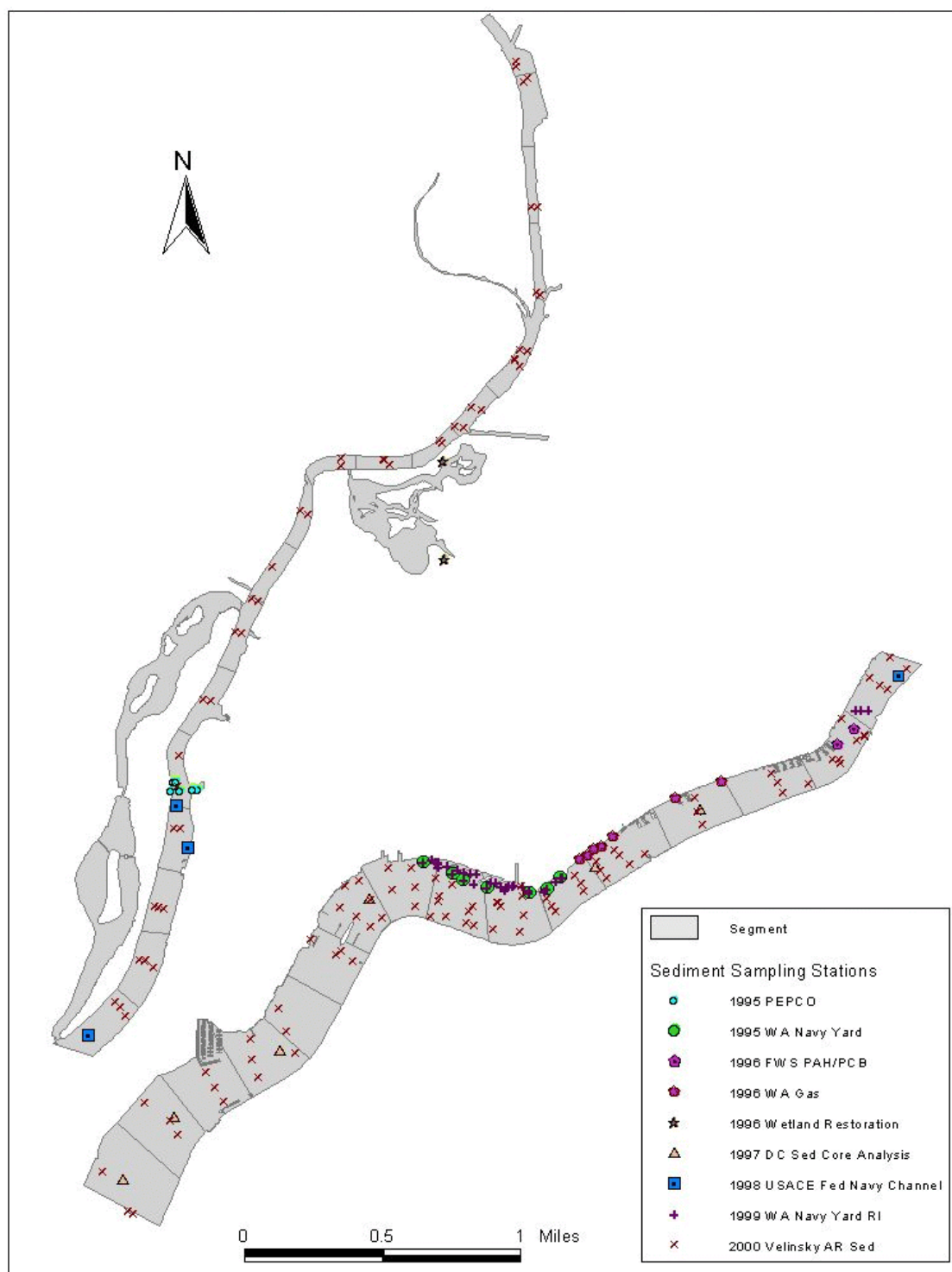


Figure 1-4. Location of Sediment Samples

CHAPTER 2: MODEL INPUTS

A variety of information must be provided to the TAM/WASP model in order to simulate the processes that determine toxic chemical concentrations in the tidal portion of the Anacostia River. Required model inputs include hourly tidal elevations at the Anacostia-Potomac confluence, daily flows discharging into the river, daily sediment and chemical loads entering the river, the dissolved phase/solid phase partition coefficients, average chemical concentrations at the Potomac boundary, and information on water and air temperature. Methods used to estimate these quantities are discussed in the sections below. The WASP water quality component of the model also requires the specification of certain additional parameters that govern simulated physical/chemical transformation processes, and determination of these additional parameters is discussed in Chapter 3: Model Calibration. Many of the required inputs are identical to those used in the TAM/WASP sediment transport model, Version 2.1, and are discussed in more detail in the report by Schultz (2001).

2.1. Hydrodynamic Model Inputs

The TAM hydrodynamic component of the TAM/WASP sediment transport model simulates water depths and flow velocities based on equations for continuity and momentum conservation (Sullivan and Brown, 1988). The hydrodynamic inputs to TAM/WASP Version 2.2 are identical to those of Version 2.1, with the exception of the inclusion of flows representing ground water inputs from the CSO sub-sheds, described at the end of this section. The primary hydrodynamic inputs are the model segment geometry, daily tidal gage heights near the downstream boundary of the model, the daily flow discharges from the two upstream tributaries, the Northeast and Northwest Branches, and daily flow discharges into each model segment from the tidal drainage area. Each of these inputs is described below and described in greater detail in the report on TAM/WASP Version 2.1 (Schultz, 2001).

The model segment geometry used in TAM/WASP Version 2.2 is identical to that used in Version 2.1. Segment widths were obtained using the GIS representation of the tidal river prepared by NOAA for the AWTa, based primarily on the National Capitol Parks - East GIS layer of the Anacostia River, and are consistent with available aerial photos of the river. Average mean-tide segment depth estimates were based on 1999 depth sounding data provided by the U.S. Army Corps of Engineers (U.S. ACE) (U.S. ACE, 1999) and an additional data set collected in the summer of 2000 for AWTa by the SPAWAR's data collection team (see Katz et al., 2000). NOAA used ESRI's Arcview Spatial Analyst software interpolation capabilities to estimate river depths at each point on a 10 ft by 10 ft grid. Average segment depths were then computed by averaging depths at all grid points within the segment.

Hourly tidal heights were obtained from NOAA for Station 8594900, "Washington, Potomac River, DC", which is located in the Washington Ship Channel. Tidal heights were downloaded from the NOAA website, in units of meters, from the vertical datum, MLLW (mean lower low water) for the tidal epoch, 1960 to 1978. Adjustments were made to this data set to account for

several periods of time for which no data was available and several days when extremely low tides caused de-watering of some model segments, a condition that cannot be handled in the current TAM/WASP framework.

Water flows into the tidal portion of Anacostia from the Northeast Branch and Northwest Branch upstream tributaries, from CSO and separate storm sewer (SS) outfalls, from the Watts Branch, Lower Beaverdam Creek and other tidal tributaries, from direct drain drainage (i.e. overland flow from areas adjacent to the river banks) and from ground water discharges. TAM/WASP model sub-sheds and sub-shed types are shown in Figure 2-1 and described in detail in the report on the TAM/WASP sediment transport model (Schultz, 2001). Flows from each of these sub-sheds are represented in TAM/WASP as daily flow inputs into each of the model segments. Flow estimates for the Northeast Branch and Northwest Branch drainage areas are obtained directly from USGS gage station data from Station 01649500 on the Northeast Branch at Riverdale Road and Station 01651000 on the Northwest Branch at Queens Chapel Road. Flow estimates for CSOs for the three-year model calibration time period (representing current conditions using 1988-90 hydrology) were obtained from DC Water and Sewer Authority (WASA) from their model developed for the Long-Term Control Plan (LTCP) (Andrea Ryon, MWCOG, private communication). CSO flow estimates for other time periods were estimated by ICPRB (see Mandel and Schultz, 2000). Flow estimates for Lower Beaverdam Creek were obtained using the HSPF model developed by Tetra Tech, Inc. for Prince Georges County (Tetra Tech, 2000). Flow estimates for the Watts Branch sub-shed and for sub-sheds drained by other minor tributaries and by the District SS system were computed using ICPRB's Watts Branch HSPF model, based on the delineation of sub-sheds as depicted in Figure 2-1, land use analysis, and precipitation data from Reagan National Airport. Daily flows for these sub-sheds were calculated as the product of the flow per unit area from each land use type, as determined from the Watts Branch HSPF model, and the area of that type within the sub-shed.

As mentioned at the beginning of this section, the TAM/WASP Toxics Screening Level Model, TAM/WASP Version 2.2, uses a hydrodynamic model identical to that used in TAM/WASP Version 2.1 with one minor change. Version 2.2 includes additional flows representing the volume of ground water from surface recharge from the CSO sub-sheds, based on predictions of baseflow per unit area of land use type from the Watts Branch HSPF model. This change has only a minor impact on model results because the added flow volume is only approximately 2% of the total. A breakdown of average annual flow contributions according to sub-shed type is given in Table 2-1, where CSO flows are WASA estimates assuming "current" system conditions. The average annual flow input percentages are quite close to the corresponding drainage area percentages, as would be expected. Note that the CSO sub-sheds are expected to contribute less flow than would be estimated from their relative areas, because a portion of the runoff from the CSO sub-shed is carried to the Blue Plains sewage treatment plant.

Table 2-1. Model Flow Input Summary

Source	Area (acres)	Area (%)	Average Annual Flow (1000 m ³)	Average Annual Flow (%)
Upstream Drainage Areas	77,800	72.0%	136,183	69.6%
Tidal Drainage Area: Watts Branch	2,470	2.2%	4,987	2.5%
Tidal Drainage Area: Lower Beaverdam	10,466	9.3%	23,390	12.0%
Tidal Drainage Area: Separate Sewers and Minor Tributaries	10,501	10.0%	20,952	10.7%
Tidal Drainage Area CSO sub-sheds Storm Overflows: Ground Water Recharge:	6,946	6.4%	5,637	2.9%
			4,468	2.3%
Total Watershed	108,183	100.0%	195,617	100.0%

2.2. Sediment Transport Model Inputs

The TAM/WASP Toxics Screening Level Model sediment transport component simulates changes in sediment concentrations in both the water column and the bed sediment by simulating the processes of advective transport, dispersive transport, deposition, and erosion. The inputs to the Toxics Screening Level Model, TAM/WASP Version 2.2, are identical to those in TAM/WASP Version 2.1, with two minor exceptions. The value specified for the advection factor in Version 2.2 is 0.25 rather than 0.0, based on examination of a dye study simulation (Schultz, 2003). The sediment concentration values specified for the Potomac boundary condition have been changed, as described in detail at the end of this section. Results of a sensitivity run investigating the differences between Versions 2.1 and 2.2 are given in Section 3.3.1. Each of the inputs to the sediment transport component of the model is described below, and described in greater detail in the report on TAM/WASP Version 2.1 (Schultz, 2001).

Average baseflow and stormflow TSS concentrations used to compute load inputs for WASP-TOXI5 were estimated from available tributary, separate storm sewer, and CSO monitoring data. Daily loads of TSS were calculated by multiplying daily stormflow and baseflow volumes by daily stormflow and baseflow concentration estimates. The model classifies sediments into three grain sizes: coarse-grained, medium-grained, and fine-grained particle size fractions. Because no monitoring data is available to determine the relative proportions of the individual grain size fractions in sediment loads entering the river, the percentage of each size fraction was estimated from the bed sediment grain size data collected by GeoSea for the AWTa (Hill and McLaren, 2000) and combined with sediment transport model calibration results. The percentages used in the model to estimate loads for each size fraction are:

Frac1 (grain sizes > 120 µm):	17%
Frac2 (grain sizes > 30 and < 120 µm):	15%
Frac3 (grain sizes < 30 µm):	68%

Daily sediment loads for the Northeast and Northwest Branches were estimated based on monitoring data collected in 1999 and 2000 as part of the WASA Long Term Control Plan program for combined sewer system overflows (CSOs) and on calibration results. Daily TSS loads from the Watts Branch tributary were estimated by based on the MWCOG Pope Branch open channel result (Shepp et al., 2000). A non-storm TSS concentration for the Watts Branch was estimated from available DC DOH routine monitoring data for station TWB01 (time period 4/20/82 to 12/9/97). Output from the Prince Georges County/TETRA TECH HSPF model of Lower Beaverdam Creek was used to generate daily TSS loads from Lower Beaverdam Creek. TSS daily load estimates for CSOs are from WASA's model developed for the LTCP, contained in a file named "cso_c2.ana", (Andrea Ryan, MWCOG, private communication). These daily load estimates are based on 1988-1990 hydrology and a CSO system "with current conditions". Storm concentrations for Nash Run, Fort Dupont, and Pope Branch use MWCOG-estimated storm concentrations for these systems based on Pope Branch monitoring data (Shepp et al., 2000), following the MWCOG designation of these sub-sheds as primarily open channel systems. TSS storm concentrations for the remaining SS and minor tributary sub-sheds, including direct drainage areas, are based on WASA LTCP provisional results (T.J. Murphy, MWCOG, private communication).

The TAM/WASP sediment transport model requires that the user input a time series of downstream boundary conditions for each of the three sediment size fractions, representing daily average water column concentrations of each of the suspended sediment size fractions in the Potomac River. Constant boundary condition values of 0 mg/L for coarse-grained sediment, 2 mg/L for medium-grained sediment, and 12 mg/L for fine-grained sediment were used for initial calibration runs of TAM/WASP Version 2.1. These values were based on an average TSS concentration of 14 mg/L from available DC DOH routine monitoring data at Station ANA29, near the confluence of the Anacostia and the Potomac River, and an average relative suspended sediment size fraction composition of 0% coarse-grained / 14% medium-grained / 86% fine-grained found in samples taken at Station ANA29 by the Academy of Natural Sciences (Schultz and Velinsky, 2001). Based on calibration results, these were changed to 0 mg/L for coarse-grained sediment, 2 mg/L of medium-grained sediment, and 20 mg/L of fine-grained sediment. In TAM/WASP Version 2.2, based on a further review of calibration results, the boundary conditions were changed back to values close to those originally used: 0.04 mg/L for coarse-grained sediment, 1.5 mg/L for medium-grained sediment, and 12 mg/L for fine-grained sediment.

Table 2-2. Model Sediment Annual Load Summary

Source	Average Annual Sediment Load (1000 kg)	Average Annual Sediment Load (%)
Upstream	27,642	89.2%
Watts Branch	655	2.1%
Lower Beaverdam	682	2.2%
Separate Sewers and Minor Tributaries	1,223	3.9%
CSOs	788	2.5%
Total Annual Load	30,990	100.0%

2.3. Partition Coefficients

Absorption onto solid material is an important process affecting the fate and transport of contaminants in the river. Contaminants in the water column that are sorbed onto sediment particles may settle to the river bottom and be buried, and contaminants in the bed sediment that are sorbed onto sediment particles may re-enter the water column if erosion occurs and sediments are re-suspended. In WASP-TOXI5, the process of adsorption is modeled using the assumption of instantaneous equilibrium partitioning, where the partitioning between the solid phase and the dissolved phase is assumed to be linear (Karickhoff, 1984), that is,

$$C_s = K_D C_w \quad (2-1)$$

where:

- C_s = concentration of contaminant on solid phase (mg/kg)
- C_w = concentration of contaminant in dissolved phase (mg/L)
- K_d = partition coefficient (L/kg)

The assumption of instantaneous partitioning is only an approximation, because it's believed that for many hydrophobic organic chemicals introduced into an aquatic environment, it may take several days to reach a solid-phase/dissolved phase equilibrium state. However, as discussed below, this assumption should be adequate given the current model data support, because in most cases discussed below, the mean K_d 's computed from baseflow data did not differ statistically from the mean K_d 's computed from stormflow data (at the 5% significance level, under the assumption that values are normally distributed). The TAM/WASP Toxics Screening Level Model uses a two-phase partitioning model, completely described by Equation 2-1. K_d 's for each constituent modeled were computed from site-specific water column data, using data, if available, from two studies, the Northeast and Northwest Branch toxics monitoring study by Gruessner et al. (1998) and the storm water runoff study by Velinsky et al. (1999). Separate baseflow and stormflow K_d 's were computed from pooled NE Branch and NW Branch

monitoring data from both studies. Also, separate baseflow and stormflow K_d 's were computed from the Anacostia River data (excluding the NE and NW Branch samples and the Potomac River samples) from the Velinsky study for the chemicals for which data was available. Sample points with non-detect or below-quantitation-limit concentrations for either the solid phase or dissolved phase were not used in the computations. Mean baseflow and stormflow K_d 's appear in Table 2-3, along with ranges, standard deviations and sample sizes. A corresponding range of values for log K_d 's found in the water quality literature is given in the last column of the table.

For metals, all mean K_d values fell within the range of reported literature values. For the Anacostia River zinc, lead and copper data, none of the baseflow mean K_d 's differed significantly, at the 5% confidence level, from the corresponding stormflow means, though it should be noted that in the Velinsky 1998 data set, no samples were actually taken during storm events, but rather on the 1st or 2nd day following a storm event. For the NE/NW Branch data, mean lead baseflow and stormflow K_d 's did not differ significantly, but the mean stormflow zinc K_d 's is significantly smaller than the mean baseflow K_d , and the mean stormflow copper K_d is significantly greater than the mean baseflow value. Finally, when mean baseflow metal K_d 's computed from the Anacostia River data were compared with those computed from the NE/NW Branch data, no statistically significant difference was found.

For the organic chemicals modeled, it was also found that there was little statistically significant difference between mean K_d values computed from stormflow and from baseflow data. PCB mean K_d values were computed for each homolog, and some means fell outside the range of reported literature values. For the Anacostia River data set, baseflow means did not differ significantly, at the 5% confidence level, from the corresponding stormflow means except in the case of homolog 6. For PAHs, the only data currently available for computing K_d values is the NE/NW Branch data set of Gruessner et al. (1998). For the 16 PAHs in this data set, none of the baseflow mean K_d 's differed significantly, at the 5% confidence level, from the corresponding stormflow mean K_d 's. For the pesticides modeled, there was no significant difference between the mean baseflow K_d 's and the mean stormflow K_d 's for cases where there were a sufficient number of sample points to carry out the statistical tests.

The summary of site-specific and literature values for K_d in Table 2-3 were used as a starting point in the calibration of the TAM/WASP Toxics Screening Level Model. Contaminants were assumed to absorb to fine-grained and medium grained particles only, with the amount of contaminants sorbed to coarse-grained material assumed to be negligible. Because contaminants are known to sorb more strongly to fine-grained material, separate K_d values were used for the fine-grained and medium-grained sediment fractions, and adjustments were made to these values during model calibration (see Chapter 3).

Table 2-3. Summary of Site-Specific and Literature K_d Values (L/kg/1000)

Constituent	Baseflow Data ^b K_d Range	Baseflow Data ^b K_d Mean	Baseflow Data ^b K_d Stdev	Baseflow Data ^b K_d Sample Size	Stormflow Data ^b K_d Range	Stormflow Data ^b K_d Mean	Stormflow Data ^b K_d Stdev	Stormflow Data ^b K_d Sample Size	Literature log K_d Values
Zinc - AR	101 - 3217	798	1035	14	10 - 1646	273	340	31	10 - 630 ^a
Zinc - NE/NW	2 - 1627	379	460	20	4 - 427	84	95	32	
Lead - AR	146 - 4370	663	1106	13	42 - 3649	434	637	30	63 - 10,000 ^a
Lead - NE/NW	3 - 7497	1342	2741	7	1 - 24,570	1813	4891	26	
Copper - AR	30 - 183	94	50	12	25 - 108	66	23	31	3 - 316 ^a
Copper - NE/NW	1 - 6152	884	1892	15	9 - 229	66	62	31	
Arsenic	NA	NA	NA	NA	NA	NA	NA	NA	
PCB Homolog 2 - AR	2 - 53	20	22	5	2 - 107	32	36	11	3.3 - 3.8
PCB Homolog 3 - AR	2 - 339	52	60	51	1 - 239	43	50	68	
PCB Homolog 4 - AR	9 - 2865	137	351	69	8 - 17,054	316	1773	92	
PCB Homolog 5 - AR	20 - 870	181	150	77	6 - 780	213	169	111	
PCB Homolog 6 - AR	56 - 714	259	128	35	42 - 1667	404	360	52	
PCB Homolog 7 - AR	88 - 16,716	765	2045	64	48 - 107	1655	10,619	100	
PCB Homolog 8 - AR	1 - 3636	559	770	23	29 - 1602	239	319	31	4.3 - 5.7
PCB Homolog 9 - AR	NA	NA	NA	0	NA	146	NA	1	5.5 - 7.2

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Constituent	Baseflow Data^b K_d Range	Baseflow Data^b K_d Mean	Baseflow Data^b K_d Stdev	Baseflow Data^b K_d Sample Size	Stormflow Data^b K_d Range	Stormflow Data^b K_d Mean	Stormflow Data^b K_d Stdev	Stormflow Data^b K_d Sample Size	Literature log K_d Values
napthalene - NE/NW	6 - 16	11	7	2	1 - 11	4	4	5	
2-methyl napthalene - NE/NW	1 - 155	35	48	9	1 - 228	39	77	8	
acenaphthylene - NE/NW	17 - 176	66	50	9	8 - 140	40	47	7	
acenaphthene - NE/NW	6 - 43	17	17	4	2 - 42	20	14	7	
fluorene - NE/NW	2 - 18	10	6	6	2 - 51	20	16	8	
phenanthrene - NE/NW	11 - 180	65	70	8	14 - 648	210	217	7	
fluoranthene - NE/NW	23 - 1598	269	447	12	37 - 405	172	136	8	
pyrene - NE/NW	11 - 3754	492	1113	11	29 - 778	309	249	8	
benz[a]anthracene - NE/NW	12 - 4150	679	1236	11	122 - 1713	686	562	7	
chrysene - NE/NW	89 - 4141	696	1101	12	217 - 1997	897	658	8	
benzo[k]fluoranthene - NE/NW	113 - 10,133	1517	2793	12	31 - 1539	785	558	5	
benzo[a]pyrene - NE/NW	41 - 12,640	2277	4392	9	250 - 1273	850	403	6	
perylene - NE/NW	35 - 1770	513	509	11	56 - 2818	699	1202	5	
indeno[1,2,3-c,d]pyrene - NE/NW	103 - 11,614	1769	3719	9	7 - 599	237	190	8	

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Constituent	Baseflow Data ^b K _d Range	Baseflow Data ^b K _d Mean	Baseflow Data ^b K _d Stdev	Baseflow Data ^b K _d Sample Size	Stormflow Data ^b K _d Range	Stormflow Data ^b K _d Mean	Stormflow Data ^b K _d Stdev	Stormflow Data ^b K _d Sample Size	Literature log K _d Values
benzo[g,h,i]perylene - NE/NW	296 - 30,669	5832	8814	12	310 - 2574	1187	955	8	
dibenz[a,h+ac]anthracene - NE/NW	48 - 3563	902	1332	6	87 - 2498	605	963	6	
cis-chlordane - NE/NW	28 - 161	62	52	6	25 - 795	186	301	6	1.7 - 5.4 ^b
nonachlor - NE/NW	31 - 332	102	100	8	42 - 1589	336	560	7	4.9 ^b
oxychlordane - NE/NW	10 - 35	20	11	4	10 - 31	16	10	4	2.9 - 4.6 ^b
heptachlor epoxide - NE/NW	5 - 190	28	61	9	2 - 98	18	35	7	1.9 - 3.0 ^b
Dieldrin - NE/NW	9 - 98	51	29	6	13 - 818	287	460	3	
4,4'-DDD - AR	NA	NA	NA	NA	NA	NA	NA	NA	
4,4'-DDD - NE/NW	NA	77	NA	1	24 - 48	36	17	2	
4,4'-DDE - AR	3 - 326	100	100	12	1 - 283	90	76	18	
4,4'-DDE - NE/NW	7 - 15	10	4	3	NA	NA	NA	NA	
4,4'-DDT - AR	243 - 326	285	59	2	41 - 347	156	136	4	
4,4'-DDT - NE/NW	NA	190	NA	1	1 - 24	10	13	3	

^a As compiled by Sigg, 1998.

^b K_d values were derived from literature K_{oc} values, where $K_d = K_{oc} * f_{oc}$ and $f_{oc} = 0.09$

2.4. Chemical Load Inputs

Water discharging into the tidal portion of the river from tributaries, sewer outfalls, and groundwater may carry with it measurable quantities of chemical contaminants. The daily quantities of these constituents entering the river, referred to as daily loads, have been estimated by ICPRB based on available toxic chemical monitoring data. Though the model has the ability to simulate differences in chemical concentrations in water discharging from each of the 34 individual tributary or outfall sub-sheds depicted in Figure 2-1, available monitoring data are limited. For this reason the model currently represents the watershed as relatively homogenous in terms of storm water quality (and baseflow/groundwater quality). For example, because the only available monitoring data for PAHs, chlordane and dieldrin are from samples taken from the upstream tributaries, the Northeast and Northwest Branches (Gruessner et al, 1998), the average concentrations computed from this data are used to estimate PAH, chlordane and dieldrin loads for all Anacostia basin sub-sheds. The situation is somewhat better for the metals included in the model, namely zinc, lead, and copper, where monitoring data is available from several sources, including the Northeast/Northwest Branch study, the recent CSO Long Term Control Plan study, recent MS4 program monitoring data, and several historical studies.

For all of the sources considered, chemical loads are estimated by using estimated average baseflow and stormflow concentrations that are assumed to not vary with respect to time. For each constituent considered in the model, the ICPRB Microsoft ACCESS input routine estimates a daily load from each of the sub-sheds depicted in Figure 2-1. For each constituent, for each sub-shed, the daily load, in units of kilograms, is estimated to be

$$\begin{aligned} \text{Daily Load} &= (\text{daily sub-shed baseflow volume}) * (\text{sub-shed baseflow concentration}) \\ &+ (\text{daily sub-shed stormflow volume}) * (\text{sub-shed stormflow concentration}) \end{aligned}$$

A summary of available storm water and baseflow monitoring data is given in Table 2-4. Information on detection limits for the primary water column data sets appears in Table 2-5. Though monitoring data for toxic contaminants are limited, loads from the upstream portion of the watershed, which accounts for approximately 70% of the water discharging into the tidal river, can be estimated from data in the Northeast/Northwest Branch study for all chemicals except arsenic. Also, as discussed above, when no other data are available, results for the upstream tributaries are extrapolated throughout the watershed. Because data from the Northeast/Northwest Branch study is heavily relied upon in the current TAM/WASP toxics chemical model simulations, a discussion of the uncertainty associated with estimates made using this data set is given at the end of this section.

2.4.1. Upstream Loads

Because the two upstream tributaries, the Northeast Branch and the Northwest Branch, drain over 70% of the Anacostia watershed, upstream loads have the potential to be a highly significant source of contamination for the tidal portion of the river. Currently, two studies contain data that can be used to help estimate upstream loads. The study by Gruessner et al. (1998) contains concentration data for metals and a variety of organic contaminants from

samples collected during six baseflow sampling events and during four storm events, for both the Northeast Branch and the Northwest Branch. During each storm event, grab samples were collected during the rising limb, the approximate peak, and the falling limb of the storm's hydrograph. For each storm, the rising limb, peak, and falling limb samples for metals were analyzed individually, but the three samples were composited before being analyzed for organics. A limited amount of Northeast and Northwest Branch data is also available from a second study (Velinsky et al., 1999).

The first two columns of Table 2-4 contain estimates of Northeast and Northwest Branch baseflow and stormflow concentrations for each of the toxic constituents, or constituent groups, modeled. For each constituent or group of constituents, separate baseflow and stormflow mean concentrations were computed by assuming that the concentration values have a log normal distribution (Gilbert, 1987), as discussed in more detail in the last section of this chapter. Baseflow metals concentrations were computed by combining baseflow data from the Gruessner et al. (1998) study and the Velinsky (date) study. Stormflow metals concentrations were computed from event mean concentrations (EMCs) for the four storm events in the Gruessner et al. (1998) data set. The metals storm data from the Velinsky study was not used because it was not deemed to be comparable. Baseflow concentrations for organics were computed from the six baseflow concentrations reported in the Gruessner study, and stormflow organics concentrations were computed from the four storm composite concentrations from the Gruessner study. To construct the time series of daily loads for input into WASP, Northeast Branch and Northwest Branch daily flow values were separated into baseflow and stormflow components using the USGS hydrograph separation program, HYSEP, using the local minimum method.

2.4.2. CSO Loads

Estimates for metals concentrations in CSO discharges are available from WASA (DC WASA, 2000a; 2000b; 2000c). Based on data collected in 1999 - 2000 for the LTCP, EMCs were computed for zinc, lead, and copper for several CSO sub-drainage areas. Data was included from the Northeast Boundary (NEB) Sewer, both from discharge treated by the swirl concentrator facility and discharge that bypassed the swirl facility. The WASA CSO EMCs are included in Table 2-4, below.

Because no CSO data exists for organic chemicals at detection limits low enough to quantify loads, concentrations of organic chemicals in CSO discharges were assumed to be the same as concentrations in the District's SS system. Therefore, for organic chemical concentrations in CSOs, mean concentrations from the District's MS4 monitoring data were used when available. Otherwise, mean values from the Northeast and Northwest Branch data set were used. Arsenic was treated similarly.

2.4.3. Lower Beaverdam Creek Loads

Stormflow and baseflow data for metals are available for Lower Beaverdam Creek from the Prince Georges County storm water monitoring program (M. Cheng, private communication). Average stormflow and baseflow concentrations values for computing zinc, lead and copper loads for Lower Beaverdam were obtained using 1998-99 data for Station 006, located in Prince

Georges County upstream of the confluence with the Anacostia. Mean stormflow concentrations for zinc, lead and copper were computed from 22 storm EMCs, and mean baseflow concentrations were computed from 3 dry weather samples.

Because no Lower Beaverdam Creek data exists for organic chemicals at detection limits low enough to quantify loads, concentrations of organic chemicals in this tributary were assumed to be the same as concentrations in the District's SS system. Therefore, for organic chemical concentrations in Lower Beaverdam, mean concentrations from the District's MS4 monitoring data were used when available. Otherwise, mean values from the Northeast and Northwest Branch data set were used. Arsenic was treated similarly.

2.4.4. Other Tributaries and Separate Storm Sewer Loads

All tidal sub-basin tributaries and separate sewer system sheds, including the Watts Branch tributary, were assumed to have identical stormflow and baseflow concentrations for all chemicals modeled. For the metals, stormflow concentrations were obtained by averaging the WASA LTCP EMCs separate sewer system results (DC WASA, 2000c) with means of the recent DC MS4 monitoring results (see Table 2-5). For arsenic, the DC MS4 monitoring results were used because the WASA EPMC-III results were all below the detection limit. For all four inorganic chemicals modeled, baseflow mean values from the Northeast/Northwest Branch data were used for baseflow concentrations.

For organic chemicals, means of recent DC MS4 monitoring data were used for stormflow concentrations when detection limits were adequate (see Table 2-5); otherwise, Northeast/Northwest Branch stormflow averages were used. Baseflow mean values from the Northeast/Northwest Branch data were used for baseflow concentrations.

Table 2-4. Summary of Available Anacostia Stormflow (SF) and Baseflow (BF) Monitoring Data

	Upstream BF/SF		WASA LTCP CSO sub-sheds SF				SS and Tribs SF		
	NE Br EMC	NW Br EMC	B St /NJ Ave EMC	Tiber Cr EMC	NEB Swirl EMC	NEB Bypass EMC	WASA LTCP EMC	DC MS4 Composite Means	LBD Cr BF/SF EMCs
Zinc (ug/l)	8/77	7/91	194	188	181	256	202	144	22/172
Lead (ug/l)	0.5/49	0.6/103	71	73	64	96	35	20	0.25/35
Copper (ug/l)	3/25	4/43	103	64	40	63	61	52	0.25/24
Arsenic (ug/l)	0.2/NA	0.2/NA	<5	<5	<5	<5	<5	1.4	
PCB1 (ng/l)	0.58/0.66	0.60/0.41						7.80	
PCB2 (ng/l)	2.63/8.81	1.90/6.13						14.97	
PCB3 (ng/l)	0.82/7.31	1.06/4.58						4.08	
PAH1 (ug/l)	0.054/0.271	0.056/0.607							
PAH2 (ug/l)	0.099/1.634	0.193/3.911							
PAH3 (ug/l)	0.044/0.945	0.097/2.631							
chlordane (ng/l)	0.81/4.49	1.19/18.93							
heptachlor epoxide (ng/l)	0.72/1.31	1.21/1.46							
dieldrin (ng/l)	0.55/0.65	0.78/1.70						0.29	
DDD (ng/l)	0.23/1.04	0.23/1.24						0.15	
DDE (ng/l)	0.52/0.07	ND/ND						0.89	
DDT (ng/l)	0.63/0.25	0.60/0.15						1.71	

Table 2-5. Sampling Methods and Detection Limits for Water Column Data Sets

Parameter	DC MS4 Program (DC SS outfalls and minor tribs)						Gruessner et al., 1998 (NE/NW Branches)	Velinsky et al., 1999 (Anacostia River)
	Sample Type	Bottle Type	Method	MDL for Method (ug/L)	MDL as in MS4 Report (ug/L)	Value Substituted for NDs (ug/L)	MDL	MDL
Metals	Composite	(1) 1000 ml Plastic HN03	U.S. EPA 200.8				Grab	Grab
Arsenic, Total				0.25	2.0	1.0		0.005
Copper, Total				1.52	2.0	N/A		0.02 ug/L (D), 0.11 ug/L (TR)
Lead, Total				0.23	2.0	N/A		0.02 ug/L (D), 0.71 ug/L (TR)
Zinc, Total				1.52	2.0	N/A		0.4 ug/L (D), 0.12 ug/L (TR)
Volatile Organic Compounds	Grab	(2) 40 ml Glass Vials Teflon Lids	U.S. EPA 624	0.5			Composite	Composite
napthalene					1.4	Only 1 detect	NA; used group average	
acenapthylene					0.8	N/A	0.010 ng/L (D), 0.500 ng/g (P)	
acenapthene					0.8	N/A	0.020 ng/L (D), 1.000 ng/g (P)	
fluorene					0.8	N/A	0.010 ng/L (D), 0.100 ng/g (P)	
phenanthrene					0.7	N/A	0.010 ng/L (D), 0.100 ng/g (P)	
fluoranthene					0.6	Only 2 detect	0.010 ng/L (D), 0.200 ng/g (P)	
pyrene					0.8	Only 1 detect	NA; used group average	
benz[a]anthracene					0.7	N/A	0.010 ng/L (D), 0.400 ng/g (P)	

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Parameter	DC MS4 Program (DC SS outfalls and minor tribs)						Gruessner et al., 1998 (NE/NW Branches)	Velinsky et al., 1999 (Anacostia River)
	Sample Type	Bottle Type	Method	MDL for Method (ug/L)	MDL as in MS4 Report (ug/L)	Value Substituted for NDs (ug/L)	MDL	MDL
chrysene					0.6	Only 1 detect	0.060 ng/L (D), 0.600 ng/g (P)	
benzo[k]fluoranthene					1.3	N/A	NA; used group average	
benzo[a]pyrene					0.6	N/A	0.010 ng/L (D), 0.700 ng/g (P)	
indeno[1,2,3-c,d]pyrene					0.6	N/A	NA; used group average	
benzo[g,h,i]perylene					0.7	N/A	NA; used group average	
dibenz[a,h]anthracene					0.6	N/A	NA; used group average	
Pesticides	Composite	(1) 1 Liter Glass Amber Teflon Lids	EPA608	0.01 to 1.7				
cis-chlordane			Values for Total Chlordane		0.34	N/A	0.009 ng/L (D), 0.080 ng/g (P)	NA
trans-nonachlor							0.010 ng/L (D), 0.100 ng/g (P)	5.2 pg/L (D), 0.1 pg/L (P)
oxychlordane							0.009 ng/L (D), 0.100 ng/g (P)	NA
Heptachlor Epoxide					0.0002	N/A	0.020 ng/L (D), 0.200 ng/g (P)	
Dieldrin					0.0002	0.001	0.020 ng/L (D), 0.200 ng/g (P)	
DDT (DDD?)					0.0004	0.0002	0.010 ng/L (D), 0.100 ng/g (P)	

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Parameter	DC MS4 Program (DC SS outfalls and minor tribs)						Gruessner et al., 1998 (NE/NW Branches)	Velinsky et al., 1999 (Anacostia River)
	Sample Type	Bottle Type	Method	MDL for Method (ug/L)	MDL as in MS4 Report (ug/L)	Value Substituted for NDs (ug/L)	MDL	MDL
DDE					0.0002	0.0001	0.010 ng/L (D), 0.100 ng/g (P)	3.3E-6 ug/L (D), 0.1E-6 ug/L (P)
DDT					0.0003	N/A	0.020 ng/L (D), 1.700 ng/g (P)	3.3E-6 ug/L (D), 0.1E-6 ug/L (P)
PCB Congeners	Composite	(2) 1 Liter Glass Amber Teflon Lids	U.S. EPA 8082 modified	0.00025 to 0.005	0.00048 to 0.0005	0.00025	0.130 ng/L (D), 0.100 ng/g (P)	No MDL (reported?) for congeners

N/A not applicable because all non-detect

Source: Nicoline Shelterbrandt

2.5. Confidence Intervals for Upstream Storm Concentration Estimates

There are relatively few storm water monitoring studies that have measured concentrations of toxic contaminants at detection limits useful for quantifying loads, especially in the case of organic chemicals. The studies that do exist typically collect samples for only a handful of storm events and a handful of baseflow events. This lack of data is primarily due to the high cost of analyzing water samples for toxic chemicals using the very sensitive methods required for load estimates. The sample sizes and the high variability of chemical concentrations in storm water result in large uncertainties in the concentration estimates that are used to compute loads. In this section, an effort is made to better understand the uncertainties associated with storm water concentrations estimates from the Northeast and Northwest Branch data.

Table 2-6 shows the results of a statistical analysis of data collected for the ICPRB Northwest and Northeast Branches study (Gruessner et al., 1998), in which four storm samples and five non-storm samples were analyzed for metals and organic contaminants using very low detection limits. This table shows the estimated mean stormflow concentrations of total PCBs, total PAHs, zinc, lead, and copper, which are used in the TAM/WASP model to compute corresponding loads to the river from the Northeast and Northwest Branch sub-sheds. The table also shows estimates of an 80% two-tailed confidence interval around each of the estimated means. Computations were done using the assumption that concentrations have a lognormal distribution, using the methods given in Gilbert (1987). This assumption cannot be tested because of the small number of sample points, but it is generally considered to be the most reasonable choice for storm water concentrations.

Though the individual uncertainty estimates themselves are highly unreliable due to the small number of sample points available, results appearing in Table 2.6 imply that estimates of concentration means based on the four sample points may be a factor of two or three or even a hundred times smaller than actual means. Alternatively, estimated concentration means may be 30% to 50% greater than actual means. Thus, the Northeast and Northwest load estimates typically have a confidence interval of roughly (mean - (30% to 50%), mean + (200% to 1000%)). These results emphasize the need in the Anacostia for storm water monitoring studies with larger numbers of sample points per sampling location. Without a substantial amount of additional data, our understanding of where and in what quantities toxic chemicals are entering the Anacostia will be limited.

Table 2-6. Statistical Uncertainty in Northeast/Northwest Branch Stormflow Concentration Means

Data (TPAH - Total PAHs TPCBs - Total PCBs BF - Baseflow samples SF - Stormflow samples)	Number of Samples	Range	Estimated Mean - (Lognormal)	Estimated Lower Limit for 80% Confidence Interval - (Lognormal)	Estimated Upper Limit for 80% Confidence Interval - (Lognormal)
TPAHs (ng/L) - NE	4	960 - 4722	2900	1900	8900
TPAHs (ng/L) - NW	4	1268 - 9113	7100	4200	65,000
TPCBs (ng/L) - NE	4	12.8 - 20.9	16.8	14.5	20.4
TPCBs (ng/L) - NW	4	2.1 - 30.7	11.0	6.1	187.2
Total Zn (µg/L) - NE	4	31 - 125	77	53	169
Total Zn (µg/L) - NW	4	37 - 210	91	59	286
Total Pb (µg/L) - NE	4	3 - 76	49	24	1392
Total Pb (µg/L) - NW	4	4 - 282	103	45	44,000
Total Cu (µg/L) - NE	4	11 - 48	25	17	55
Total Cu (µg/L) - NW	4	4 - 80	43	21	481

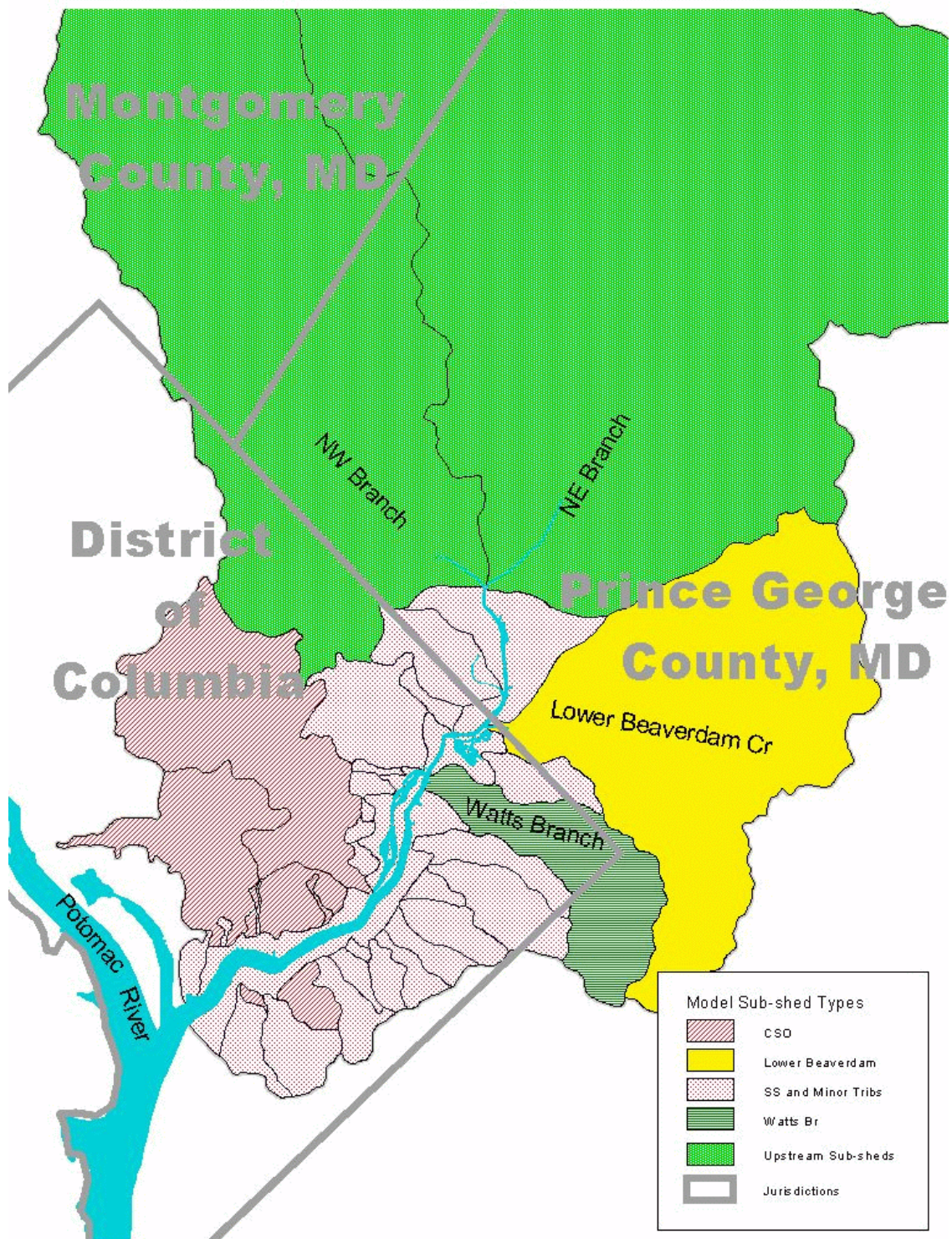


Figure 2-1. TAM/WASP Model Sub-sheds and Sub-shed Types

CHAPTER 3: MODEL CALIBRATION/VERIFICATION

In the calibration/verification process, predictions of the TAM/WASP Toxics Screening Level Model were compared with available Anacostia River data, and, if necessary, adjustments were made to a limited number of model input parameters to improve model performance. A description of the general strategy used to calibrate and verify the model is given in the first section of this chapter. A discussion of how data was processed for model calibration and verification purposes, including water column concentration data, surficial bed sediment concentration data, and fish tissue data, is given in Section 3.2. Calibration/verification results for the six sub-models are given in Section 3.3. Finally, an evaluation of model sensitivity runs and performance is given at the end of this chapter.

3.1. General Calibration Strategy

The TAM/WASP Toxics Screening Level Model is based on the already-calibrated TAM/WASP sediment transport model (Schultz, 2001). The primary inputs new to the toxic chemicals component of the model are the chemical load inputs, the solid phase/dissolved phase partition coefficients (K_d 's), and chemical concentrations at the Potomac River boundary. Additional inputs that have an effect on model predictions are parameters governing air/water exchange and degradation of chemicals. As discussed below, site-specific data was used to estimate chemical load inputs and K_d 's for initial model runs. In some cases, K_d 's and/or loads were adjusted during the calibration process to produce a better match in model predictions and observed concentrations. Potomac River boundary conditions were based on data when available, or otherwise, were selected based on calibration run results. Inputs governing air/water exchange and degradation were based on values found in the literature, and were not adjusted in the calibration process.

Initial model runs were done using mean stormflow and mean baseflow chemical concentrations computed from monitoring data, summarized in Table 2-4, to estimate daily loads, and mean K_d 's computed from Anacostia River baseflow water column data, given in Table 2-3. For chemicals where no Anacostia River K_d 's were available, Northeast/Northwest Branch mean baseflow K_d 's were used. These initial model runs simulated the deposition of contaminated sediment to the river bottom over a six-year time period. 1988 through 1990 hydrology, considered in several studies to represent a typical "wet" year, "dry" year, and "average" year in terms of precipitation (Mandel and Schultz, 2000), was used to generate model flows, and this three-year simulation was run twice, using the WASP model's "RESTART" option, to simulate processes over a six-year time period. These model runs began with initial conditions that simulated a "clean" sediment bed, i.e. with chemical concentrations initially set equal to zero in all bed sediment segments. The model uses WASP's variable bed volume option (IBEDV = 1) and a surficial sediment layer depth of 1 cm in order to make the bed sediment concentrations responsive to inputs on an annual time scale. Model predictions for last day of the six-year run for the 35 main channel sediment segments were compared to averaged bed sediment data for these segments (see Section 3.2.1 below) to determine whether or not the initial load estimates were producing the observed magnitude of contamination in the river's sediment bed. In a number of cases, namely, for zinc, copper, chlordane, and dieldrin, predicted contaminant

concentrations matched observed concentrations reasonably well, and it was decided that loads estimated from the available monitoring data were reasonable. In other cases, the model predictions produced significantly lower concentrations in the sediment bed than is observed and in one case the model predicted a higher concentration than is observed. Given the uncertainty in the model load estimates (see Section 2.5), it is not unexpected that load estimates may be 50% too high, or be a factor of 2 or 3 or more too low. Therefore, in cases where it was necessary, the model stormflow and baseflow chemical concentrations were increased or decreased to obtain a reasonable match of model predictions to bed sediment contamination data.

In the second phase of the calibration process, the model was run to simulate daily water column concentrations for time periods in which data was available. Water column data is available for 1998 for zinc, lead, copper, PCBs, p,p DDE and p,p DDT. For these chemicals, model predictions for the dissolved phase and for the total (dissolved + particulate) phase concentrations were compared with available data. In some cases, model K_d values were adjusted to produce a better fit to the dissolved concentration data. For chemicals for which no water column calibration data was available, model predictions were compared to predictions of ambient concentrations based on fish tissue data and bioaccumulation factors (see Section 3.2.2).

As mentioned above, partition coefficients used in the model were based on site-specific data, and in some cases were adjusted in the calibration process. TAM/WASP Version 2.2 can simulate the absorption of chemical contaminants onto the fine-grained and medium-grained sediment fractions but not onto the coarse-grained fraction. This seems reasonable because it is known that contaminant concentrations are generally higher in finer-grained sediments. K_d 's for organic contaminants are known to be proportional to the sediment's fraction of organic carbon (foc), and higher foc values in the Anacostia have been found to be correlated with smaller average sediment grain sizes (Velinsky and Ashley, 2001). Also, because of their higher mass to surface area ratio, coarse-grained sediments necessarily will contain lesser quantities of contaminants on a mass chemical per mass sediment basis. For this reason, K_d 's for the fine-grained sediment fraction were initially set equal to mean K_d 's computed from baseflow data. K_d 's for the medium-grained fraction were set to be a factor of 1/4 of the fine-grained K_d 's. If adjustments were made to K_d 's during the calibration process, the same adjustment factor was applied to both the fine-grained and the medium-grained K_d 's. Results of runs to investigate the sensitivity of model predictions to changes in K_d 's are presented below in the sections on the metals model calibration, the arsenic model calibration, and the PCB model calibration.

3.2. Discussion of Calibration Data

Three types of data are used in the model calibration/verification process: water column chemical concentration data, bed sediment chemical concentration data, and fish tissue chemical concentration data. The use of the water column concentration data is relatively straightforward. Model predictions of daily water column concentrations (both total and dissolved) are compared with concentrations measured in water samples collected from the river. However, in the case of the bed sediment concentration data and the fish tissue data, a certain amount of analysis must be done before values can be obtained that are useful for comparison with model results. These analyses are described in

Sections 3.2.1 and 3.2.2, below.

3.2.1. Estimation of Bed Sediment Segment Concentration Averages

Bed sediment concentrations in the tidal sub-basin are based on the Velinsky and Ashley (2001) data set and several historical data sets available in the AWT/NOAA database (NOAA, 2001), as described in Section 1.4.3 of this report. The average sediment concentration in each WASP segment (Table 3-1) were estimated from the data points by Inverse Distance Weighted (IDW) spatial interpolation and zonal statistics using Environmental Systems Research Institute (ESRI) software products, including ArcMap and Spatial Analyst.

Spatial interpolation is a method that allows estimating values for locations where no measured values are available and can be used to create a continuous value surface from data collected at discrete locations (i.e. points) or to explore spatial patterns in point-sampled data. IDW interpolation is a spatial interpolation method that uses weighted moving averages within an area of influence to predict values of grid cells. IDW assumes that each data point has a local influence that diminishes with distance. To predict a value at an unknown location, IDW looks at the measured values surrounding the prediction location and assigns weights that are inversely proportional to the distance to the prediction location, raised to a user-specified power. At a higher power, the nearest data points exert the most influence on the prediction location, creating an interpolated surface that is more detailed but less smooth; whereas at a lower power, the influence of more distant points is increased, creating a surface that is smoother but less detailed. A power of two is commonly used. Because the interpolated surface is a weighted average of data points, the predicted grid cell values cannot be greater than the highest or less than the lowest input value.

There are two common approaches for defining the neighborhood search area: a) fixing the search radius and allowing interpolation between a variable number of data points or b) specifying the number of data points (i.e. nearest neighbors) within a variable search radius to be used for the interpolation. The choice of method depends on the spatial distribution of the data points and the presence of outliers. The fixed radius approach may fail to find neighbors when the data points are spaced too far apart, and as a result the interpolated surface may be discontinuous. The nearest neighbor method, on the other hand, yields a continuous output surface, but the points may be so far apart that the results may be misleading.

Based on sensitivity analyses, ICPRB determine that by using a grid cell size of three meters, a power of two, with six nearest neighbors, IDW predicted the interpolated surface fairly accurately for most of the chemicals. Zonal statistics was then used to estimate the average chemical concentrations in each WASP segment from the grid values. With ArcMap's zonal statistics function, a statistics (e.g., mean sediment concentration) can be calculated for each zone (e.g., WASP segment) in a zone data set based on the values of a value grid (e.g., IDW interpolated sediment concentration grid).

Estimated sediment concentrations of the modeled constituents for the tidal portion of the Anacostia River are shown in comparison to the Thresholds Effects Limit (TEL) and Probable Effects Limit (PEL) (source: Buchman, 1999) or as standard deviations when TEL and PEL were not available in Figures 3-1 to 3-14.

Table 3-1. Average Segment Sediment Concentrations (ng/g dry weight)

Segment	Zinc	Lead	Copper	Arsenic	PCB1	PCB2	PCB3	PAH1	PAH2	PAH3	Total Chlordane	Heptachlor Epoxide	Dieldrin	p,p DDD	p,p DDE	p,p DDT
1	104679	27632	18949	3.3	10.6	19.9	6.2	603	2203	2214	5.4	0.55	0.42	1.5	1.1	0.9
2	124477	28217	42377	3.3	30.1	50.6	16.0	1361	4990	5020	11.9	1.05	1.00	2.9	2.3	1.5
3	263314	57277	46411	3.3	11.4	57.3	33.7	1835	9191	8398	17.9	1.71	1.71	6.5	4.5	3.7
4	252762	57894	49262	3.3	7.5	58.2	31.2	1862	9531	8517	22.8	1.56	1.80	7.5	5.0	3.3
5	220396	51242	48727	3.3	9.9	58.5	28.6	1429	7450	7700	27.6	1.48	3.19	9.2	6.8	2.8
6	251804	58821	60110	3.4	16.7	73.5	34.8	1840	9509	10137	33.8	1.85	5.57	11.1	8.4	3.8
7	199068	49074	38050	3.6	23.7	70.3	23.6	1403	6468	6577	20.2	1.19	3.68	7.6	4.7	2.8
8	172548	37771	33165	3.7	38.5	73.8	18.8	941	4201	4029	13.5	1.18	2.74	11.6	3.7	7.2
9	143411	31352	45854	3.4	22.1	47.5	16.0	689	3547	3114	11.8	0.90	1.36	5.2	3.0	2.5
10	182699	49629	40791	3.2	15.0	56.5	22.0	853	5036	4313	16.4	0.07	1.51	6.5	5.2	2.3
11	189770	43959	51912	3.1	16.5	61.4	25.7	856	4843	4885	18.3	0.01	1.81	7.3	6.3	2.3
12	276725	74125	61978	3.2	21.2	83.9	31.8	1648	7752	9321	24.7	0.01	3.12	11.5	8.9	5.9
13	152750	70512	44137	3.4	10.2	54.8	22.8	1363	4308	4481	9.4	0.28	1.73	6.5	4.0	3.6
14	209450	69465	153845	3.5	33.6	193.5	86.2	667	2299	2376	14.8	0.13	1.42	16.3	12.8	2.3
15	228644	64500	50833	3.2	55.7	326.3	56.7	754	3874	3771	31.9	0.88	1.69	24.1	18.5	4.5
16	270671	74100	62671	4.3	37.6	233.6	51.2	1494	7868	7615	28.8	1.35	1.89	13.4	10.9	4.1
17	234474	73119	51049	4.2	23.8	103.8	31.3	1498	6739	6075	20.3	1.12	1.49	11.6	12.8	7.0
18	230543	63765	48914	3.7	19.0	83.3	28.4	1311	6837	6564	25.5	1.12	2.07	15.9	14.6	4.4
19	276549	88963	67469	3.4	25.4	109.2	42.1	1801	7898	8406	22.4	0.92	3.39	15.2	12.3	3.9
20	270636	92822	65887	4.2	24.8	100.4	34.0	8780	12006	8134	22.8	0.36	3.39	19.1	21.3	4.0
21	232664	96506	51703	4.3	25.9	113.2	32.8	2668	8204	6805	30.5	1.06	3.62	31.0	33.2	10.0
22	213175	114978	52246	5.6	21.4	117.1	33.7	2221	7989	7181	29.6	1.19	2.50	16.9	5.5	15.5
23	210906	122075	53822	6.1	23.7	149.0	51.5	5607	15325	10981	35.1	1.03	2.66	14.7	9.7	6.0
24	254232	69501	70521	8.7	17.2	119.1	40.6	16224	27260	16423	24.6	0.90	2.29	11.9	4.2	17.9
25	327815	93010	90149	5.4	20.9	114.9	54.5	4944	9232	7914	25.5	0.89	3.08	11.0	8.8	4.7
26	328992	98175	92868	6.9	20.1	124.6	59.9	2210	7793	7399	30.5	0.92	3.16	13.2	8.7	12.1
27	329065	100405	97437	6.7	17.3	209.1	139.2	4932	9902	8398	29.0	1.35	2.66	11.7	7.6	17.2

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Segment	Zinc	Lead	Copper	Arsenic	PCB1	PCB2	PCB3	PAH1	PAH2	PAH3	Total Chlordane	Heptachlor Epoxide	Dieldrin	p,p DDD	p,p DDE	p,p DDT
28	495290	202866	145160	7.5	39.1	732.6	567.9	4007	11164	11110	34.3	0.66	2.72	23.5	27.7	32.7
29	555629	220679	142153	7.5	57.6	380.0	175.0	1911	7774	8981	38.9	0.28	3.04	22.9	30.1	40.3
30	306851	101132	93611	7.5	14.0	108.3	44.1	1323	4689	5333	18.2	0.21	0.99	8.0	13.5	34.7
31	338812	97763	100016	7.5	12.7	83.1	42.3	930	4210	5063	18.7	0.22	1.29	6.2	10.7	50.3
32	314355	80083	88489	7.5	13.4	82.9	52.3	795	3668	4507	16.1	0.31	1.80	10.1	12.3	27.2
33	276090	63430	79101	7.5	8.6	50.3	28.4	547	2369	3023	11.6	0.28	1.18	21.8	9.1	13.7
34	240419	49007	72135	7.5	6.6	42.6	27.0	447	1831	2442	7.8	0.28	0.81	5.6	7.6	11.9
35	213742	41502	62960	7.5	7.1	47.9	24.7	424	1635	2074	6.7	0.28	0.79	3.3	7.6	9.9

3.2.2. Estimates of Ambient Water Column Concentrations From Fish Tissue Data

For some of the chemicals modeled in this study, no water column concentration data is currently available for comparison with model predictions. An alternative method based on fish tissue chemical concentrations and bioconcentration factors is available to estimate ambient water column concentrations. When water column data is available, water column estimates based on fish tissue concentrations can be used for calibration verification. The calculation involves dividing the average fish tissue concentration by the bioconcentration factor to obtain a projected water column concentration:

$$TC/BCF = WC * 1000$$

Where:

TC = tissue concentration in mg/kg (equivalent to mg/L)

BCF = U.S. EPA Bioconcentration Factor in L/kg

WC = water column concentration (estimated) in mg/L

Multiply by 1000 to obtain ug/L

Fish tissue concentrations are available (USGS Fred Pinkney, private communication) for several of the modeled chemicals. The data set consists of four fish species (bluegill, carp, channel catfish, and largemouth bass) for a total sample size of 25. Bioconcentration factors (BCF) were obtained from U.S. EPA for all modeled chemicals except PAHs, heptachlor epoxide, and zinc. Estimated water column concentrations are provided in Table 3-2.

Table 3-2. Estimated Water Column Concentration for Selected Chemicals Based on Fish Tissue Concentrations

Chemical	BCF	Est. Water Column Conc (ug/L)
Zn	na	x
Pb	49 (U.S. EPA, 1980f)	1.44
Cu	36 (U.S. EPA, 1980d)	16.93
As	44 (U.S. EPA, 1980b)	1.99
PCB	31,200 (U.S. EPA, 1980g)	2.89E-02
PAH	na	x
Chlordane	14,100 (U.S. EPA, 1980c)	6.62E-03
Heptachlor epoxide	na	x
Dieldrin	4,670 (U.S. EPA, 1980a)	2.34E-03
p,p DDD	53,600 (U.S. EPA, 1980e)	6.20E-04
p,p DDE	53,600 (U.S. EPA, 1980e)	1.72E-03
p,p DDT	53,600 (U.S. EPA, 1980e)	5.19E-05

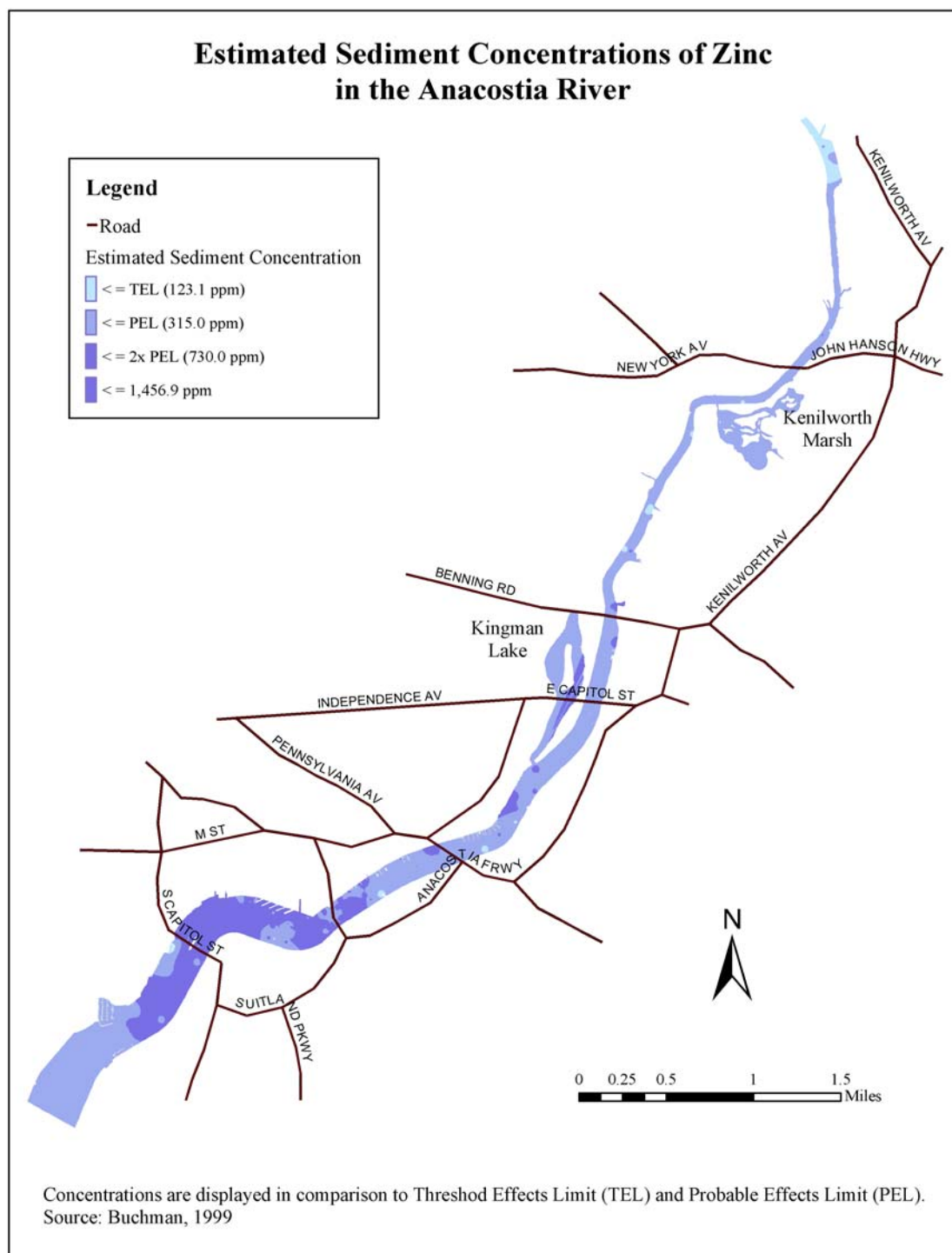


Figure 3-1. Estimated zinc concentrations (ppm) in Anacostia River surficial bed sediments

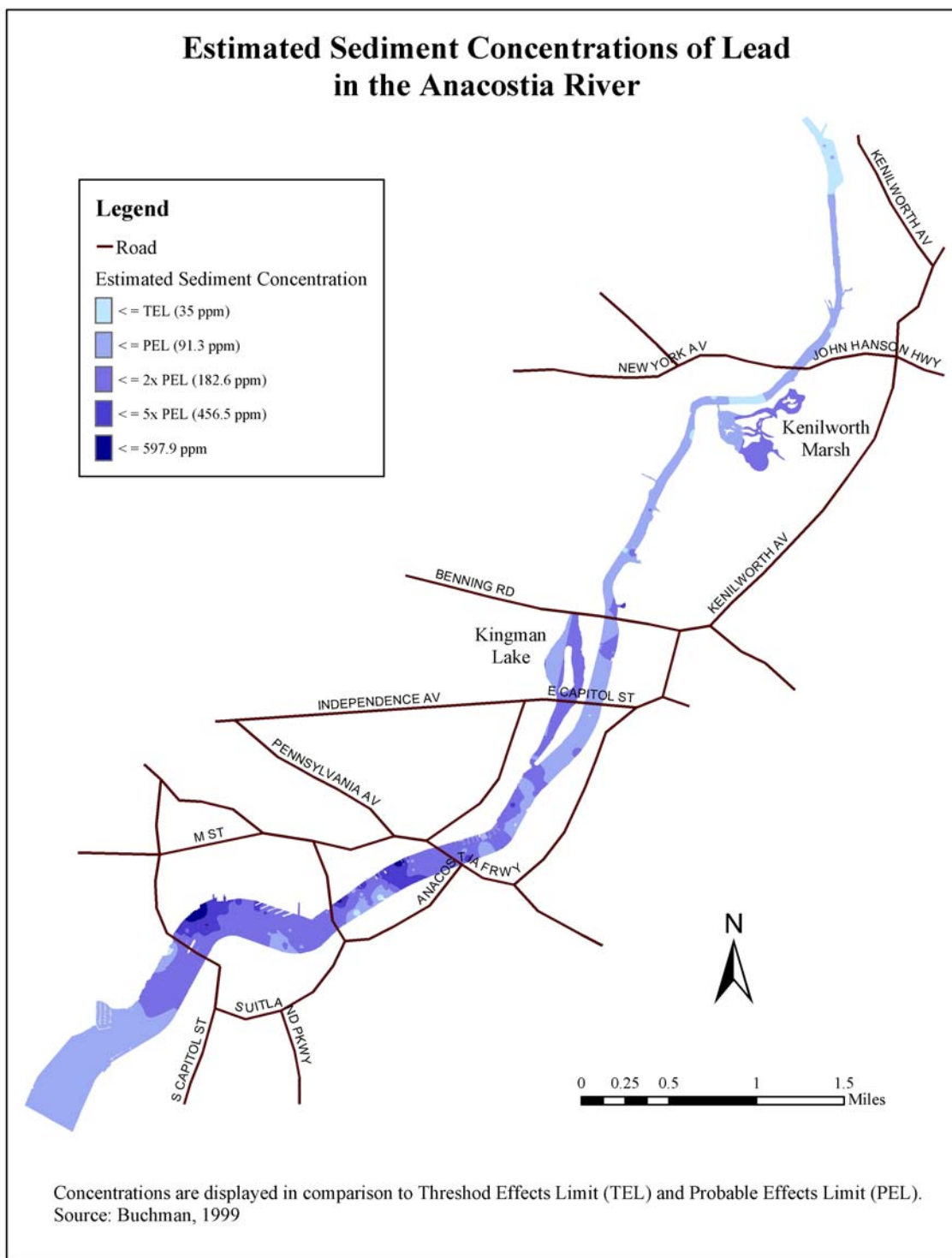


Figure 3-2. Estimated lead concentrations (ppm) in Anacostia River surficial bed sediments

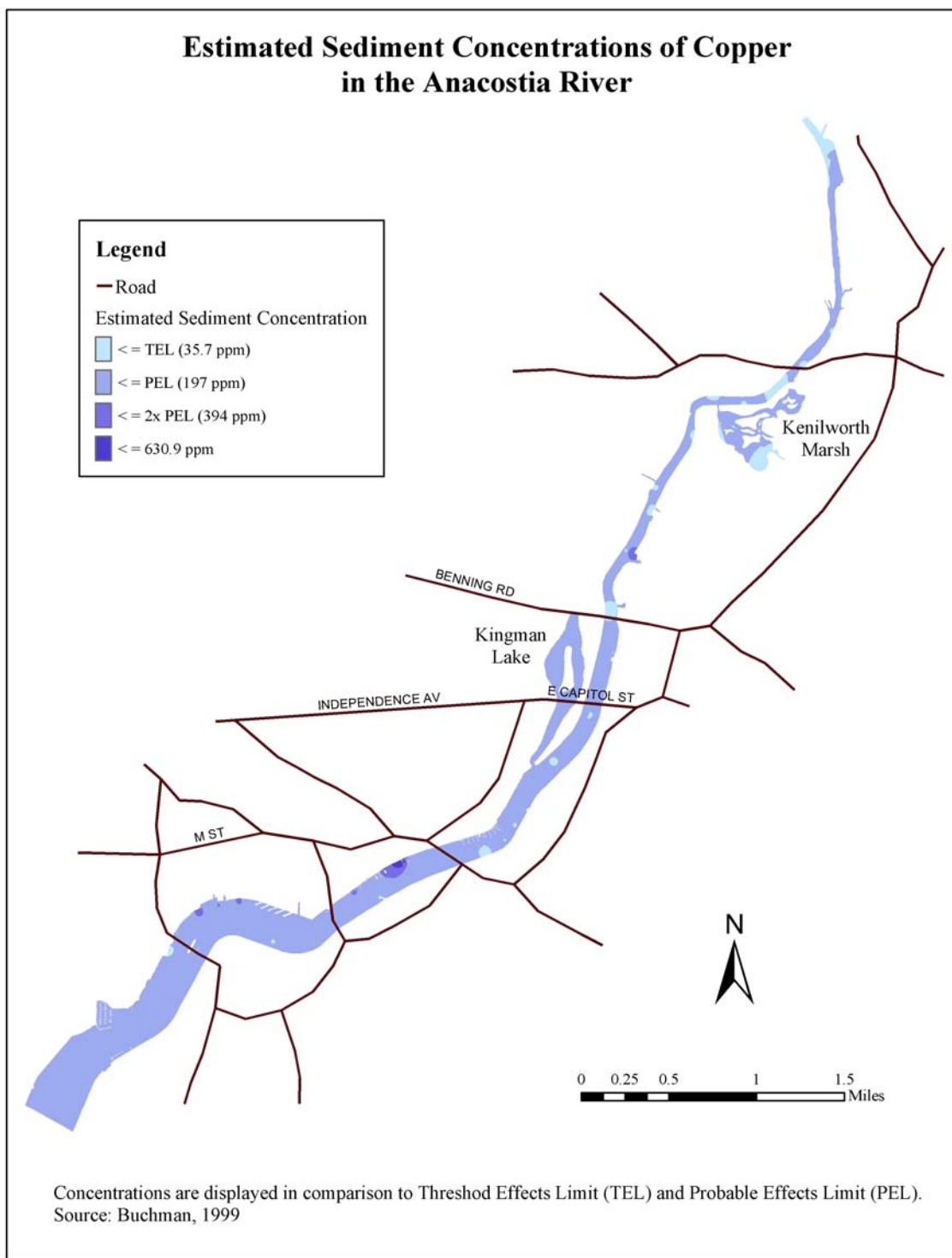


Figure 3-3. Estimated copper concentrations (ppm) in Anacostia River surficial bed sediments

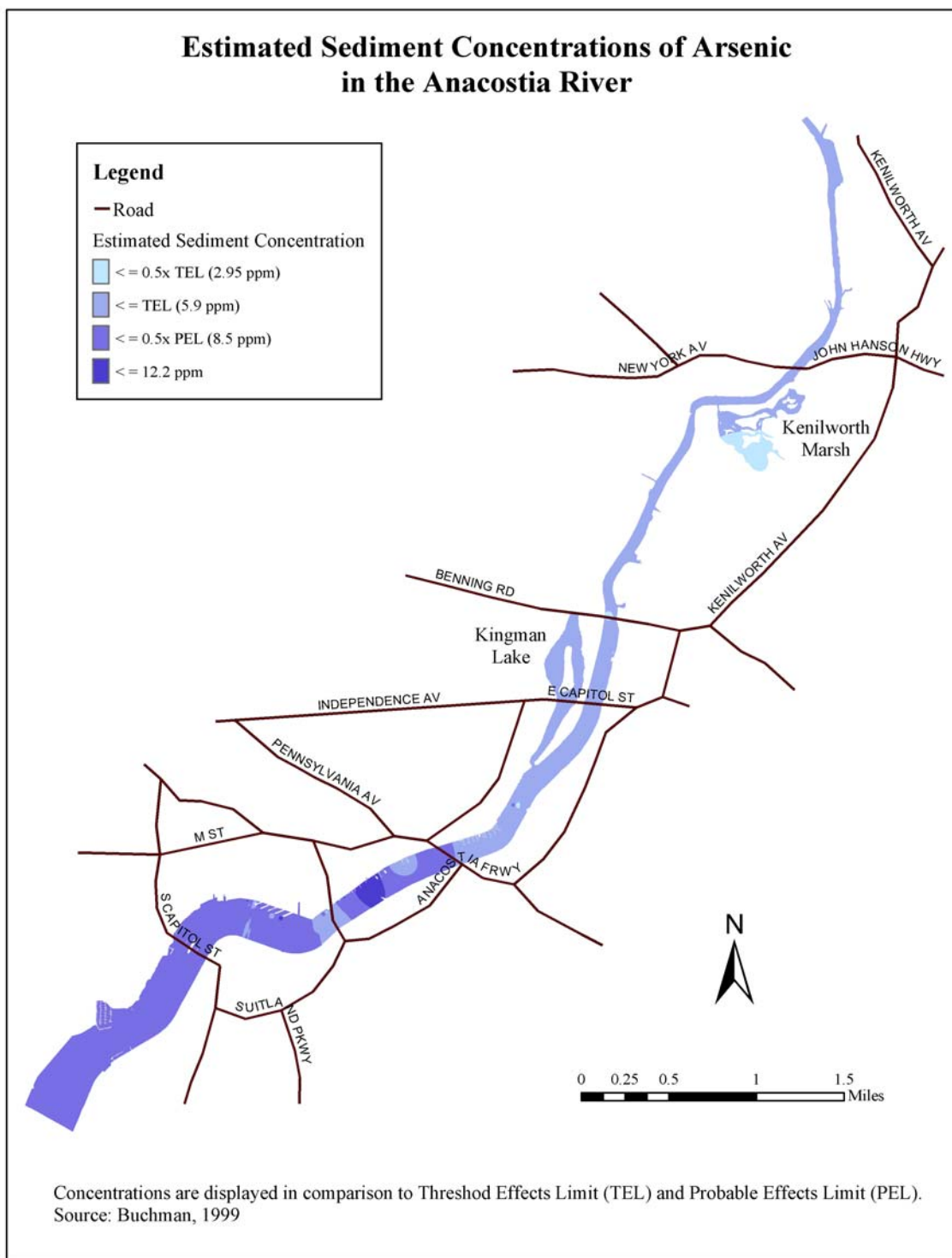


Figure 3-4. Estimated arsenic concentrations (ppm) in Anacostia River surficial bed sediments

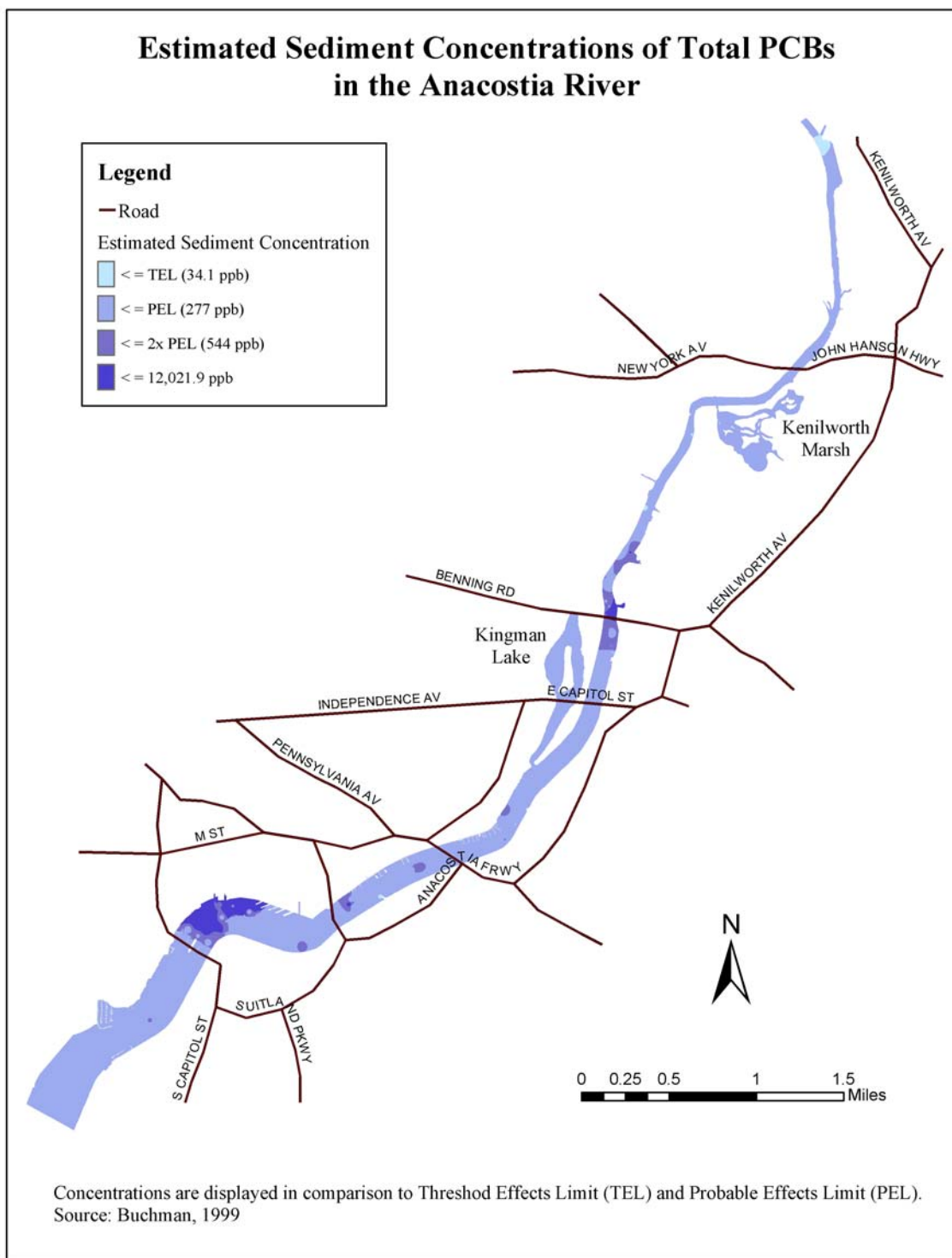


Figure 3-5. Estimated total PCBs concentrations (ppb) in Anacostia River surficial bed sediments

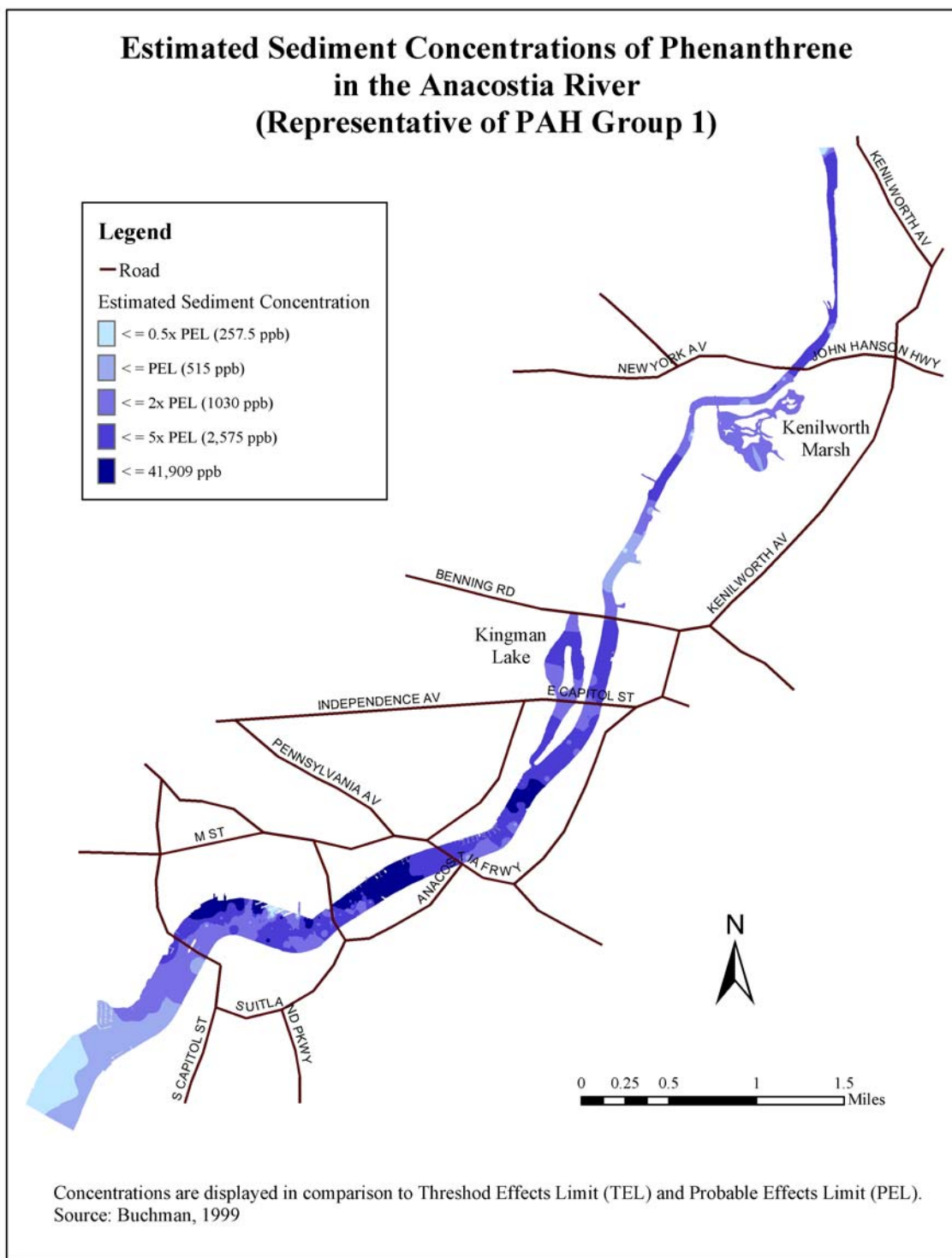


Figure 3-6. Estimated phenanthrene (representative of PAH Group 1) concentrations (ppb) in Anacostia River surficial bed sediments

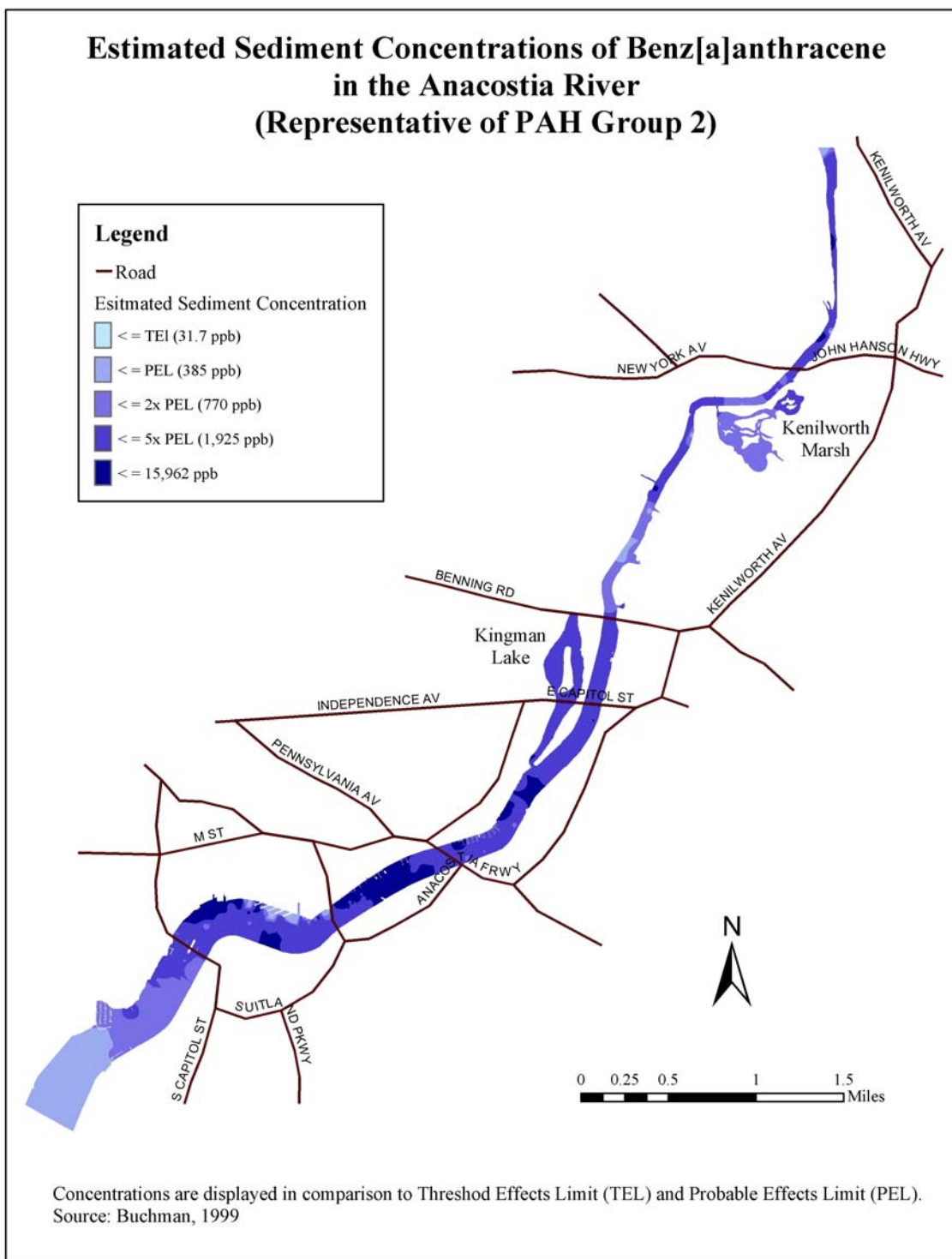


Figure 3-7. Estimated benz[a]anthracene (representative of PAH Group 2) concentrations (ppb) in Anacostia River surficial bed sediments

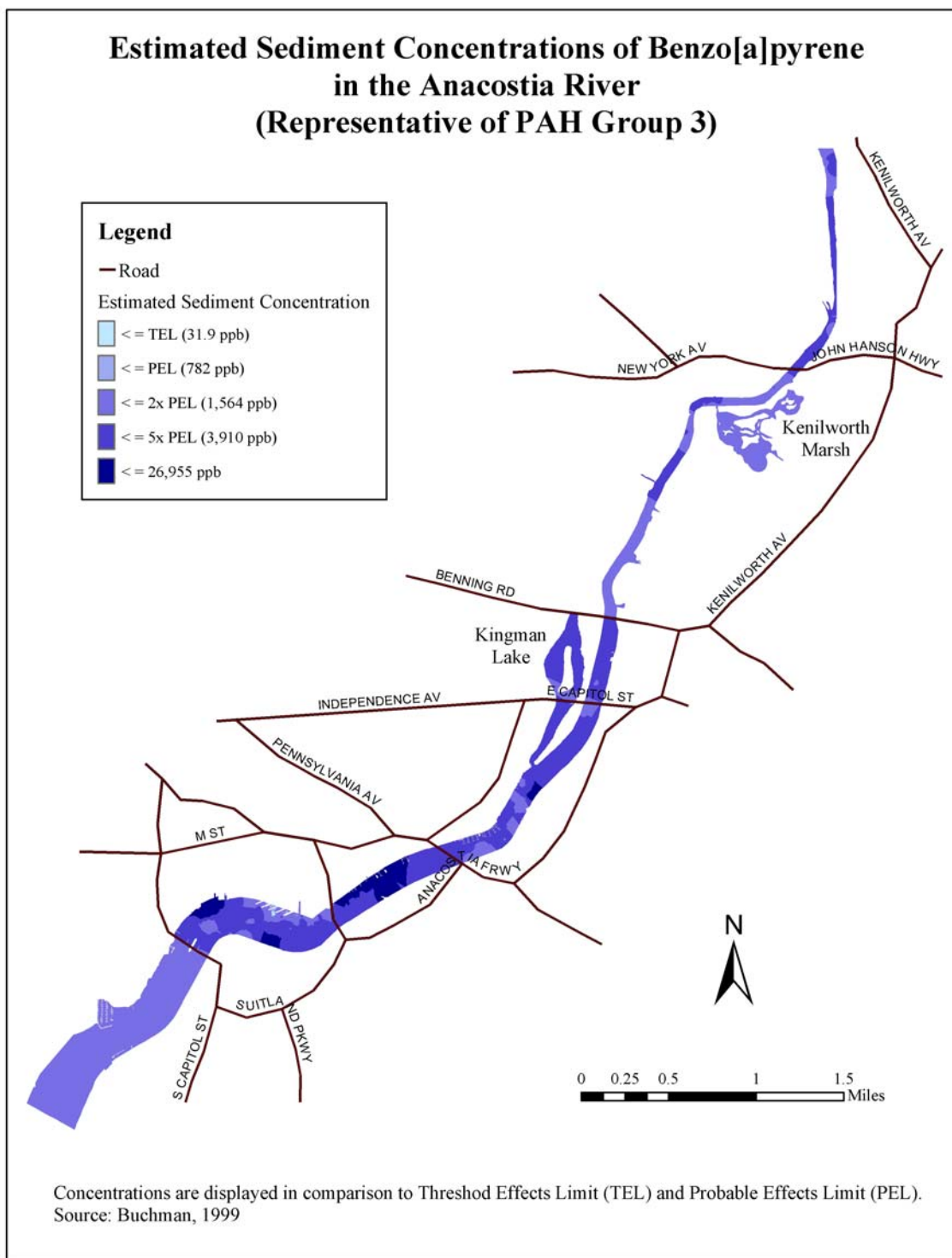


Figure 3-8. Estimated benzo[a]pyrene (representative of PAH Group 3) concentrations (ppb) in Anacostia River surficial bed sediments

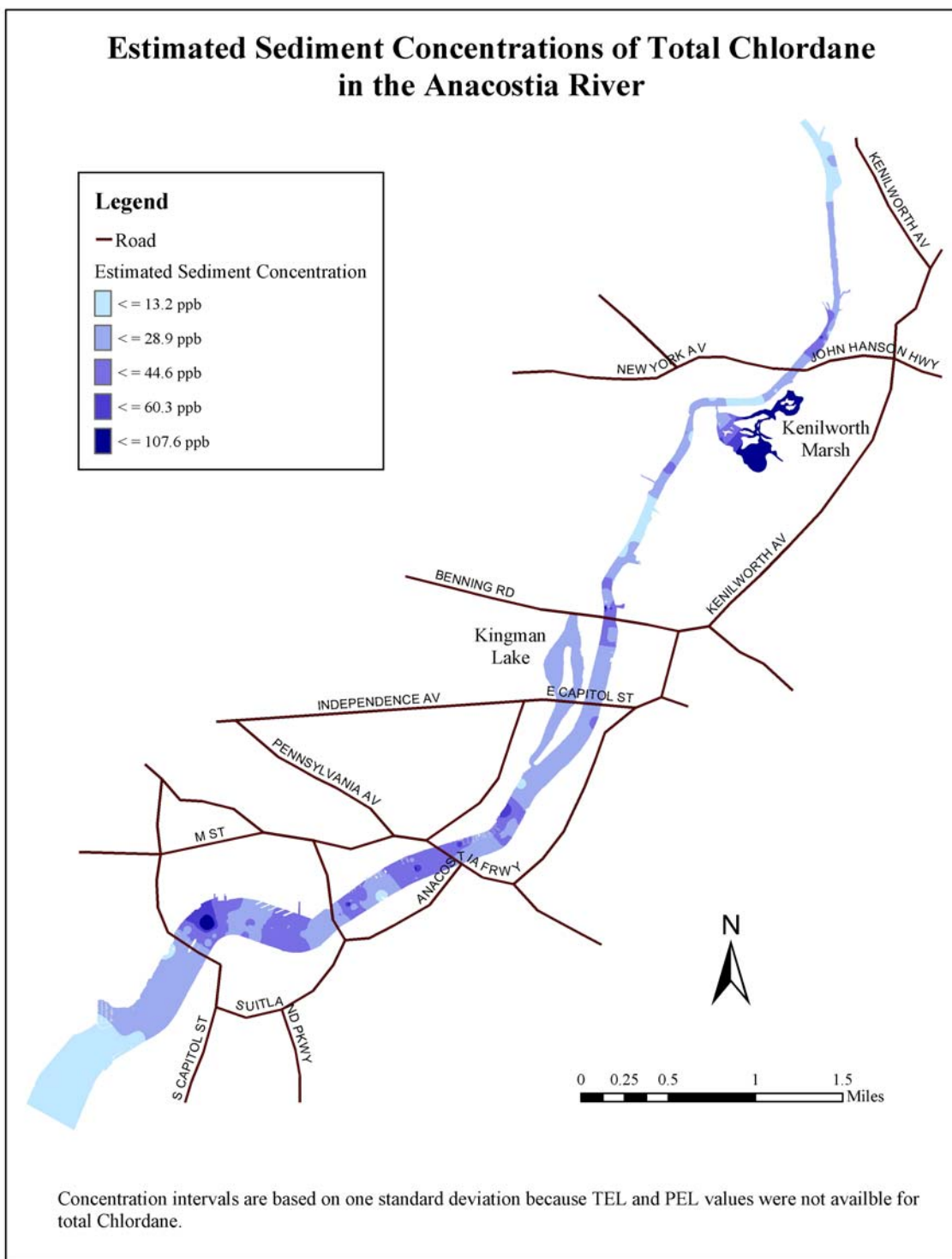


Figure 3-9. Estimated total chlordane concentrations (ppb) in Anacostia River surficial bed sediments

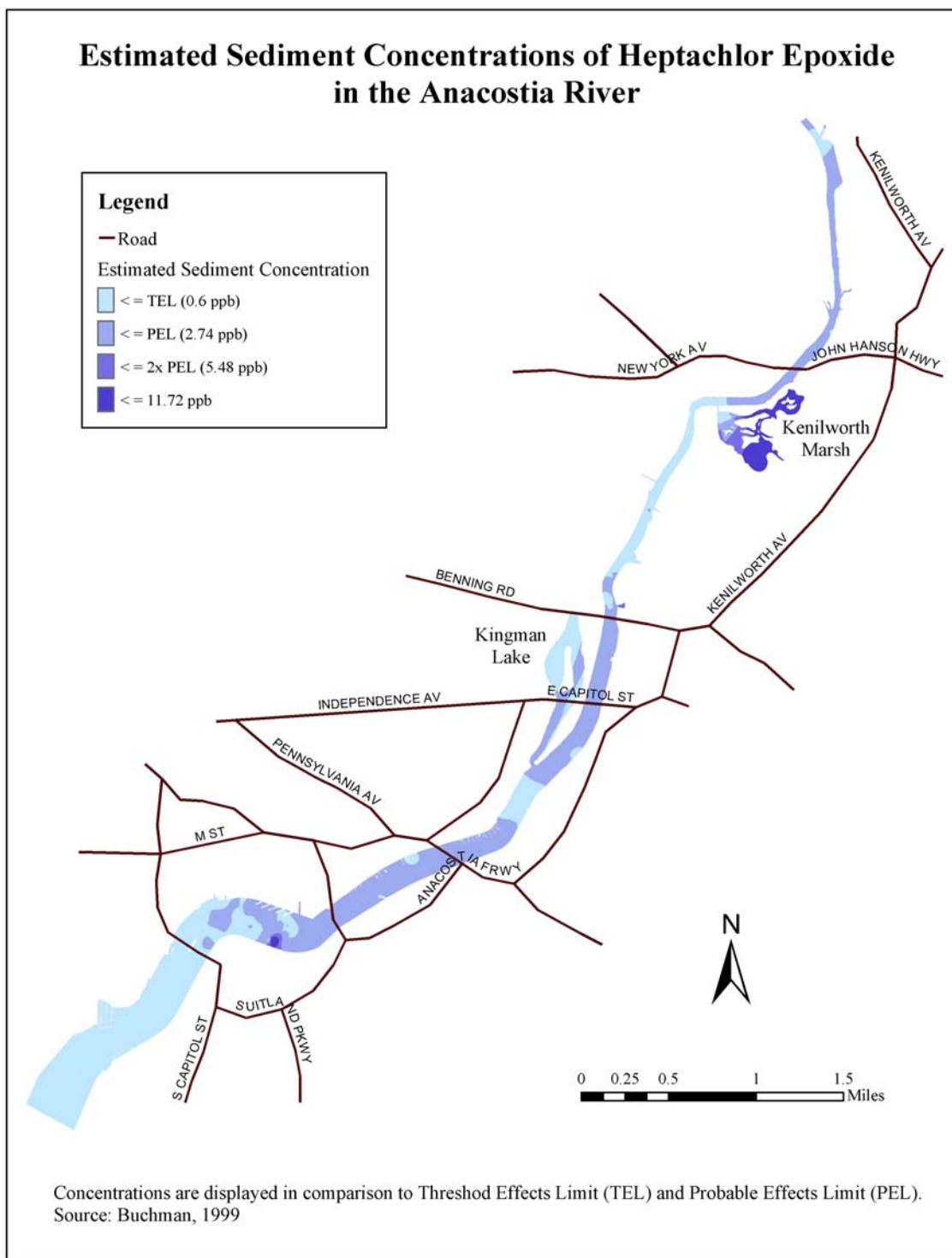


Figure 3-10. Estimated heptachlor epoxide concentrations (ppb) in Anacostia River surficial bed sediments

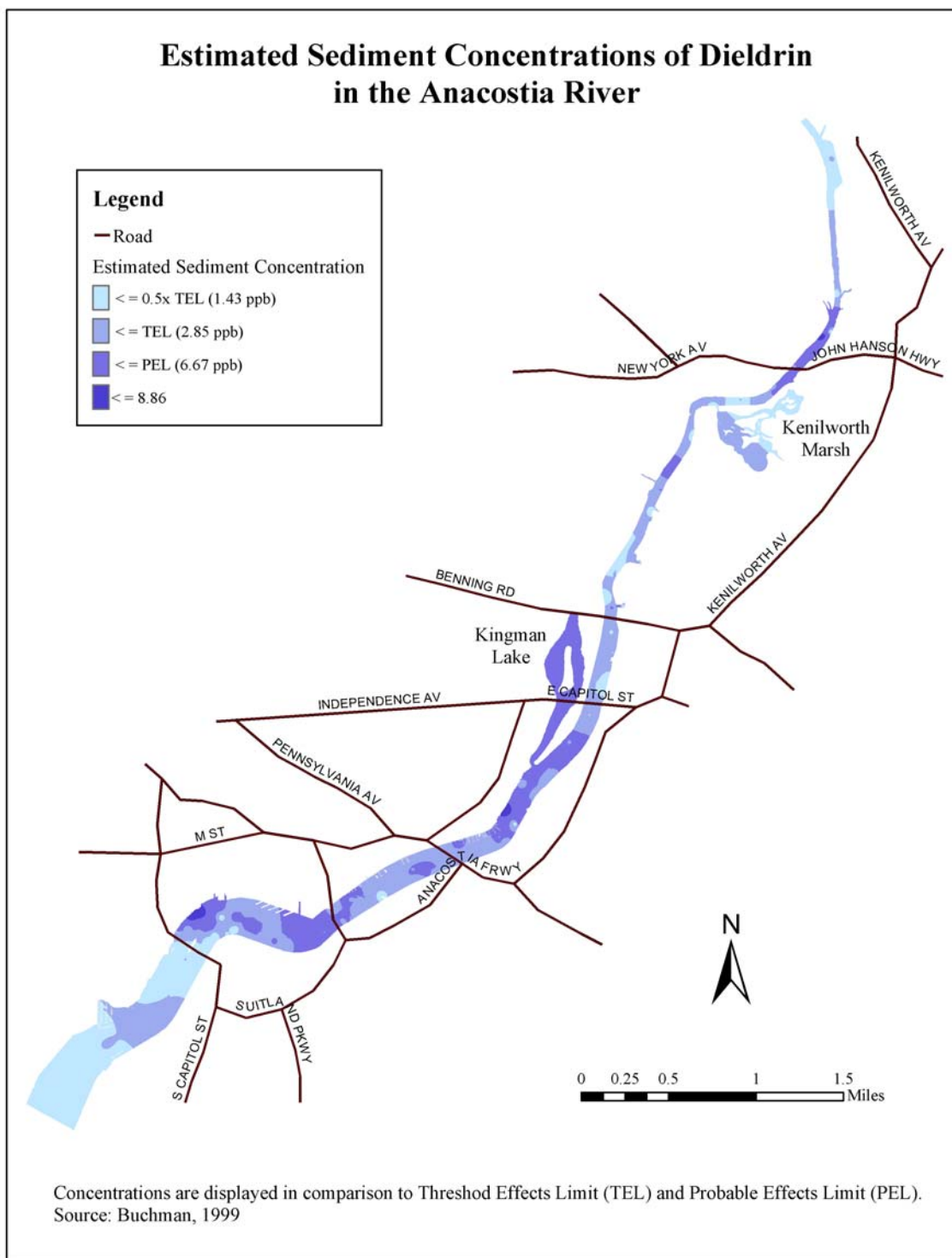


Figure 3-11. Estimated dieldrin concentrations (ppb) in Anacostia River surficial bed sediments

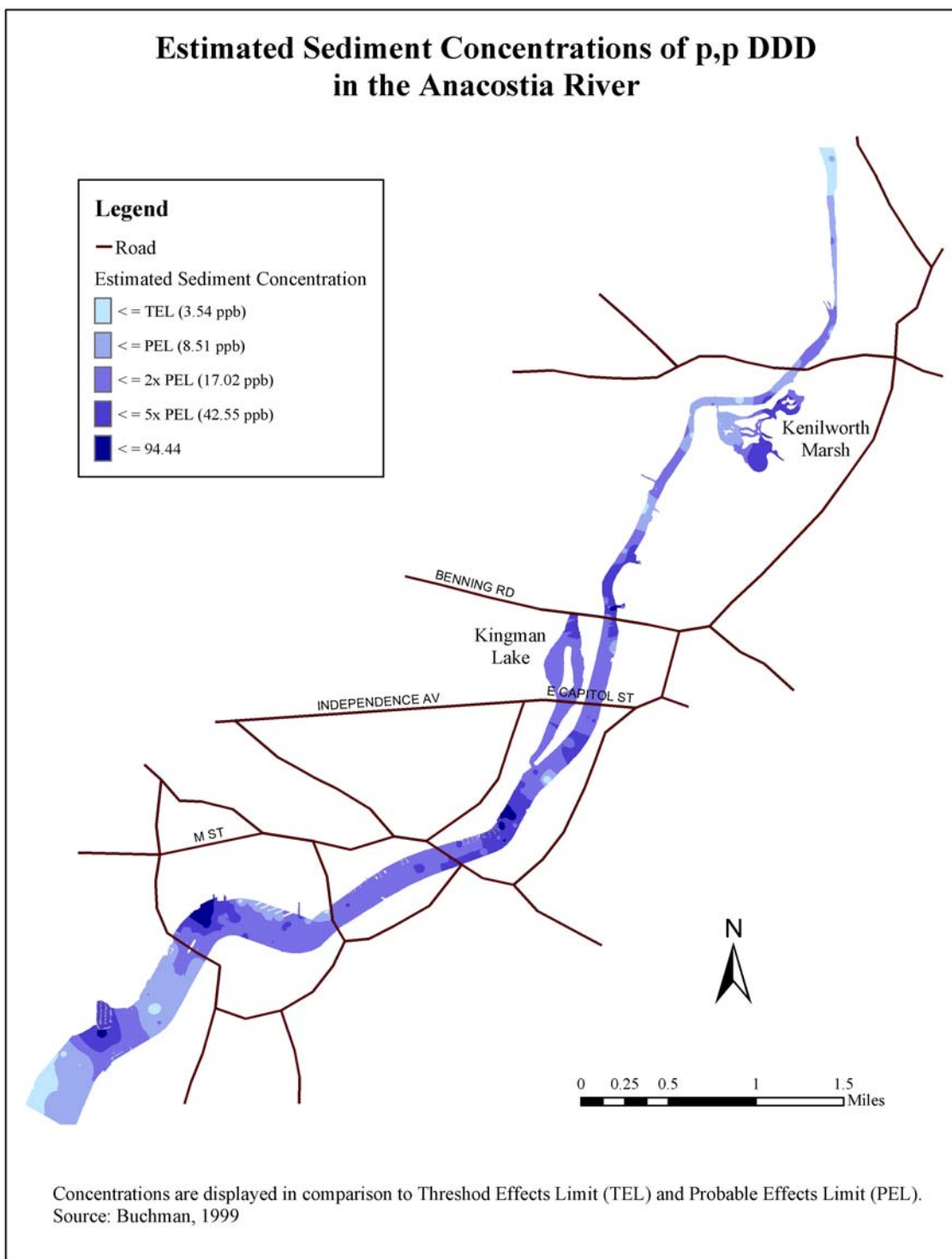


Figure 3-12. Estimated p,p DDD concentrations (ppb) in Anacostia River surficial bed sediments

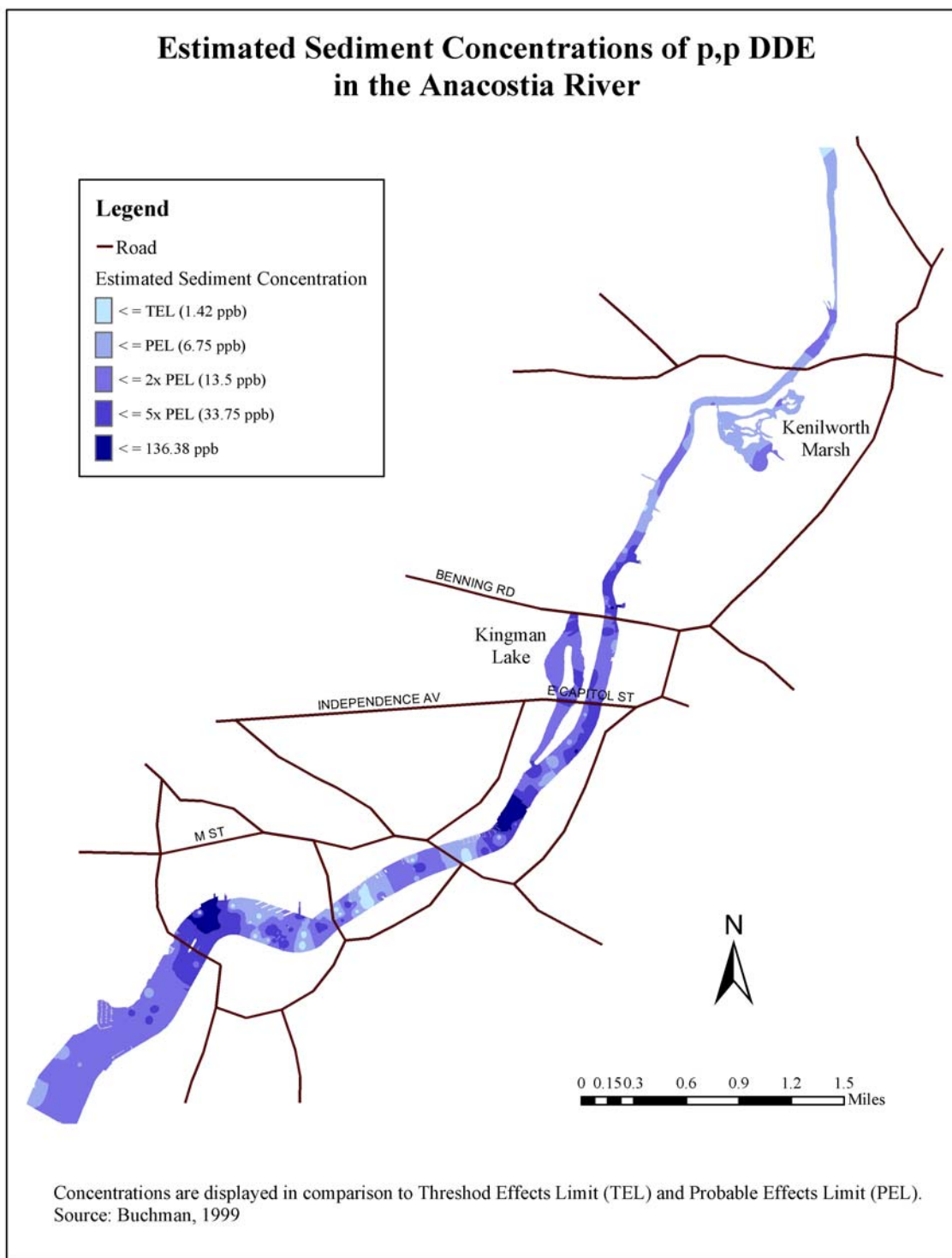


Figure 3-13. Estimated p,p DDE concentrations (ppb) in Anacostia River surficial bed sediments

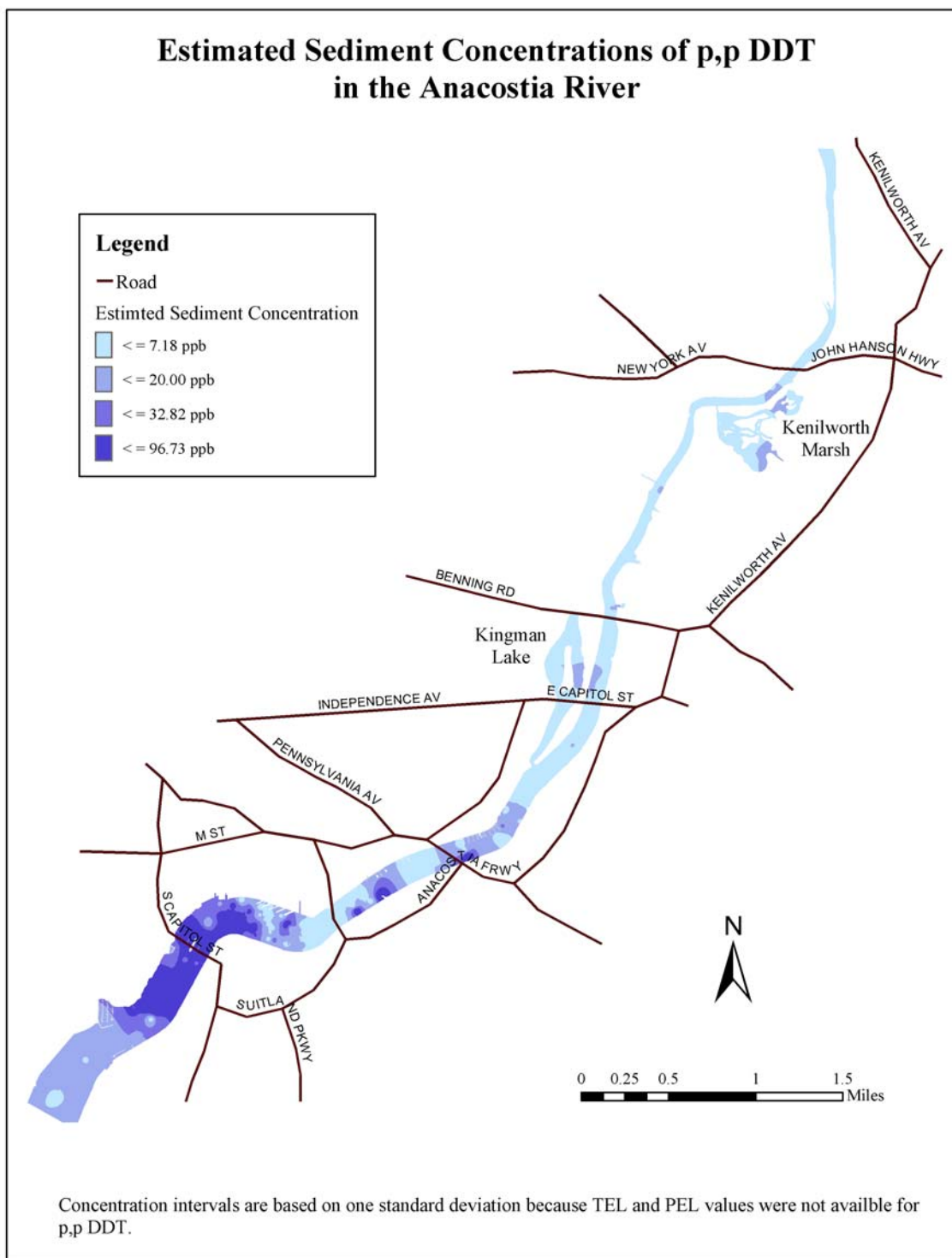


Figure 3-14. Estimated p,p DDT concentrations (ppb) in Anacostia River surficial bed sediments

3.3. Calibration Results

Discussions of the calibration/verification of the six TAM/WASP Toxics Screening Level Model sub-models appear below.

3.3.1. Metals Sub-Model

Model Description

The TAM/WASP sub-model for metals (Metals1), has been configured to simulate the loading, fate and transport of total zinc, total lead, and total copper. The only fate and transport process simulated, in addition to advection and dispersion, is absorption to the medium and fine-grained sediment fractions. Chemical speciation of these three metals is not simulated due to lack of data support. However, data support for the Metals1 model is otherwise quite reasonable.

Input Parameters

Proposed distribution coefficients for zinc, lead, and copper are given in Table 3-3. These values are based on an analysis of water column data available in Velinsky et al. (1999), and on water column calibration results. Initial model calibration runs were made using the mean K_d values computed from baseflow Anacostia River data (Table 2-3). Then K_d values for zinc and lead were adjusted downward in order to better match observed dissolved water column concentrations. Model boundary conditions at the Potomac confluence, also given in Table 3-3, were set using the mean of four pre-storm Potomac River concentrations reported in the Velinsky 1998 water column data set.

Data to estimate load inputs of zinc, lead and copper to the tidal Anacostia is available from the Gruessner study of upstream loads (Gruessner et al., 1998), the WASA LTCP study of District CSO and separate sewer system pollutant concentrations (DCWASA, 2000), the District's MS4 program storm water monitoring data (Nicoline Shelterbrandt, private communication), and the Prince Georges county monitoring program (Dr. Mow Soung Cheng, private communication). Values used in the calibration are given in Table 3-4. As discussed below, upstream lead concentrations used in load computations were reduced by 50% based on calibration results.

Model Results

Calibration/verification runs were made to compare model predictions with the bed sediment data collected in 2000 by Velinsky and Ashley (2001) and the water column data collected in 1998 in the storm water runoff study by Velinsky et al. (1999). A comparison of model predictions (last day of 6 year run) versus estimated bed sediment segment concentration averages, shown in Figure 3-15, suggests that the metals model accounts well for total zinc and copper mass inputs into the tidal portion of the Anacostia. Model predicted lead bed sediment concentrations on the other hand are too high. Because predicted lead concentrations are high even in the far upstream segments, ICPRB suggests that upstream lead loads be reduced by a factor of $\frac{1}{2}$ for the final lead calibration (see Table 3-4). Model predicted lead bed sediment concentrations with the $\times 0.5$ upstream load reductions are also shown in Figure 3-15.

Predicted total metals water column concentrations versus water column data from Velinsky et al. are shown in Figures 3-16 through 3-18. Figure 3-17, which shows water column total lead concentrations, is based on upstream lead loads reflecting the suggested factor of $\frac{1}{2}$ reduction. Predicted water column concentrations match the limited amount of available data quite well, with the exception of segment 8, adjacent to Kenilworth Marsh. The fairly close match between predicted and measured total lead concentrations in the water column lends support to the appropriateness of the factor of $\frac{1}{2}$ load reduction for upstream lead. Figures 3-19 through 3-21 show predicted dissolved water column concentrations versus water column data from Velinsky et. al (1999).

Results of a mass balance analysis for metals appear in Table 3- 5 and Figure 3-22. According to model load estimates, the upstream tributaries account for the majority of the metals found in the sediment bed of the tidal river. Lower Beaverdam Creek contributes a higher proportion of the metals load than would be expected from its relative land area. Approximately $\frac{1}{3}$ of the metals discharged into the tidal portion of the Anacostia are eventually exported to the Potomac River.

Model Sensitivity Analysis

Results of metal model sensitivity runs appear in Figures 3-23 through 3-38. Because all of the TAM/WASP Toxic Screening Level sub-models have been constructed using a similar framework, many of the results of the metals sensitivity runs are also applicable to other sub-models.

Initial values for the partition coefficients for the fine-grained sediment fraction were based on mean values computed from site-specific baseflow water column data (Table 2-3). (These values were then sometimes adjusted during the calibration process based on model predictions of dissolved phase concentrations.) Because the computed K_d 's were highly variable, sensitivity runs were done to investigate changes in model predictions when all metals K_d 's were multiplied by 4, or all metals K_d 's were multiplied by $\frac{1}{4}$. Bed sediment results are shown in Figure 3-23. Water column results appear in Figures 3-16 to 3-21.

Though it is known that fine-grained sediments typically have higher fractions of organic carbon and larger partition coefficients than coarser-grained sediments, in the TAM/WASP Toxics Screening Level Model, the ratio of the K_d 's for the medium-grained sediment fraction to the K_d 's for the fine-grained sediment fraction was rather arbitrarily set equal to $\frac{1}{4}$. Runs to investigate the sensitivity of model results to this choice were done. Figures 3-24 to 3-30 show results of model runs using a ratio of medium-grained to fine-grained sediment K_d 's of 1 and of $\frac{1}{10}$.

The underlying hydrodynamic and sediment transport components of TAM/WASP Version 2.2 are identical to those of Version 2.1 with three exceptions, discussed in Sections 2.1 and 2.2 of this report. Figures 3-31 through 3-33 show the results of a sensitivity test done to compare metals predictions of the two model versions.

Because water from the Potomac enters the Anacostia every day during the rising tide, chemical concentrations in the Potomac River have an effect on concentrations in the Anacostia. In the TAM/WASP Toxics Screening Level Model, Potomac River chemical concentrations are set at

constant values based on a handful of measured values. In the case of some chemicals, no Potomac River data was available and Potomac River boundary conditions are based on calibration results. Figures 3-35 to 3-38 show the results of two sensitivity runs done to investigate changes in the metals sub-model predictions if estimated Potomac boundary conditions were halved or doubled.

Table 3-3. WASP Input Parameters for Metals1 Sub-Model

Process	Parameter	Units	Zinc	Lead	Copper	Source
<i>Adsorption:</i>						
	K_d for fine-grained sediment	L_w/kg_s	420,000	400,000	94,000	Based on 1998 water column data ^a
	K_d for medium-grained sediment	L_w/kg_s	100,000	100,000	23,000	Taken to be 1/4 times K_d for fine-grained sediment, based on best professional judgement.
<i>Downstream boundary condition:</i>						
	Typical Potomac concentration	ug/L	4.0	0.3	2.0	Mean of non-storm concentrations at Potomac confluence, 1998 water column data ^a

^a Computed from data in Velinsky et al. (1999)

Table 3-4. Concentrations Used to Compute Metals1 Sub-Model Calibration Run Input Loads (ug/L)

Source	Zinc Orig	Suggested Zinc Multiplier	Zinc Draft Final	Lead Orig	Suggested Lead Multiplier	Lead Draft Final	Copper Orig	Suggested Copper Multiplier	Copper Draft Final	Data Source/ Comment
NW Br Base	7	x 1	7	0.6	x 0.5	0.3	4	x 1	4	Gruessner et al. (1998) 1995-96 data and Velinsky et al. 1998 data - mean of 10 values.
NW Br Storm	91	x 1	91	103	x 0.5	51.5	43	x 1	43	Gruessner et al. (1998) 1995-96 data - mean of 4 EMC's.
NE Br Base	8	x 1	8	0.5	x 0.5	0.25	3	x 1	3	Gruessner et al. (1998) 1995-96 data and Velinsky et al. 1998 data - mean of 10 values.
NE Br Storm	77	x 1	77	49	x 0.5	24.5	25	x 1	25	Gruessner et al. (1998) 1995-96 data - mean of 4 EMC's.
LBD Creek Base	22	x 1	22	0.25	x 1	0.25	0.25	x 1	0.25	PG Co. 1998-99 monitoring data at site 006; mean of 3 values.
LBD Creek Storm	172	x 1	172	35	x 1	35	24	x 1	24	PG Co. 1998-99 monitoring data at site 006. Mean of 24 EMCs.
SSTrib Base/ GW	7.5	x 1	7.5	0.6	x 1	0.6	3.5	x 1	3.5	Using mean of NE and NW Branches baseflow values.

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Source	Zinc Orig	Suggested Zinc Multiplier	Zinc Draft Final	Lead Orig	Suggested Lead Multiplier	Lead Draft Final	Copper Orig	Suggested Copper Multiplier	Copper Draft Final	Data Source/ Comment
SSTrib Storm	173	x 1	173	28	x 1	28	57	x 1	57	Average of WASA EPMC-III value and recent 2002 DC MS4 monitoring mean.
B St. NJ Ave/ Tiber Cr CSO	191	x 1	191	72	x 1	72	83	x 1	83	WASA LTCP monitoring: average of B St. NJ Ave. and Tiber Creek results.
NE Swirl and Bypass	256	x 1	256	96	x 1	96	63	x 1	63	WASA LTCP monitoring program result.
All other CSOs	213	x 1	213	80	x 1	80	76	x 1	76	WASA LTCP monitoring program estimate.

Table 3-5. Average Annual Load Contributions and Losses by Source for Calibrated Metals1 Sub-Model

	Zinc		Lead		Copper	
Loads/Losses	kg	%²	kg	%	kg	%
Upstream	6,927	49	2,744	64	2,698	61
SS Tribs	2,072	15	341	8	696	16
LBD	3,591	25	719	17	493	11
Watts	505	4	83	2	170	4
CSOs	1,061	7	389	9	342	8
Total Input ¹	14,156	100	4,276	100	4,399	100
Export to Potomac	-4,630	-33	-1,500	-35	-1,651	-38

¹ Total Input is the sum of loads from upstream, SS Tribs, LBD, Watts and CSOs.

² % represents the percentage of total input (sum of all loads).

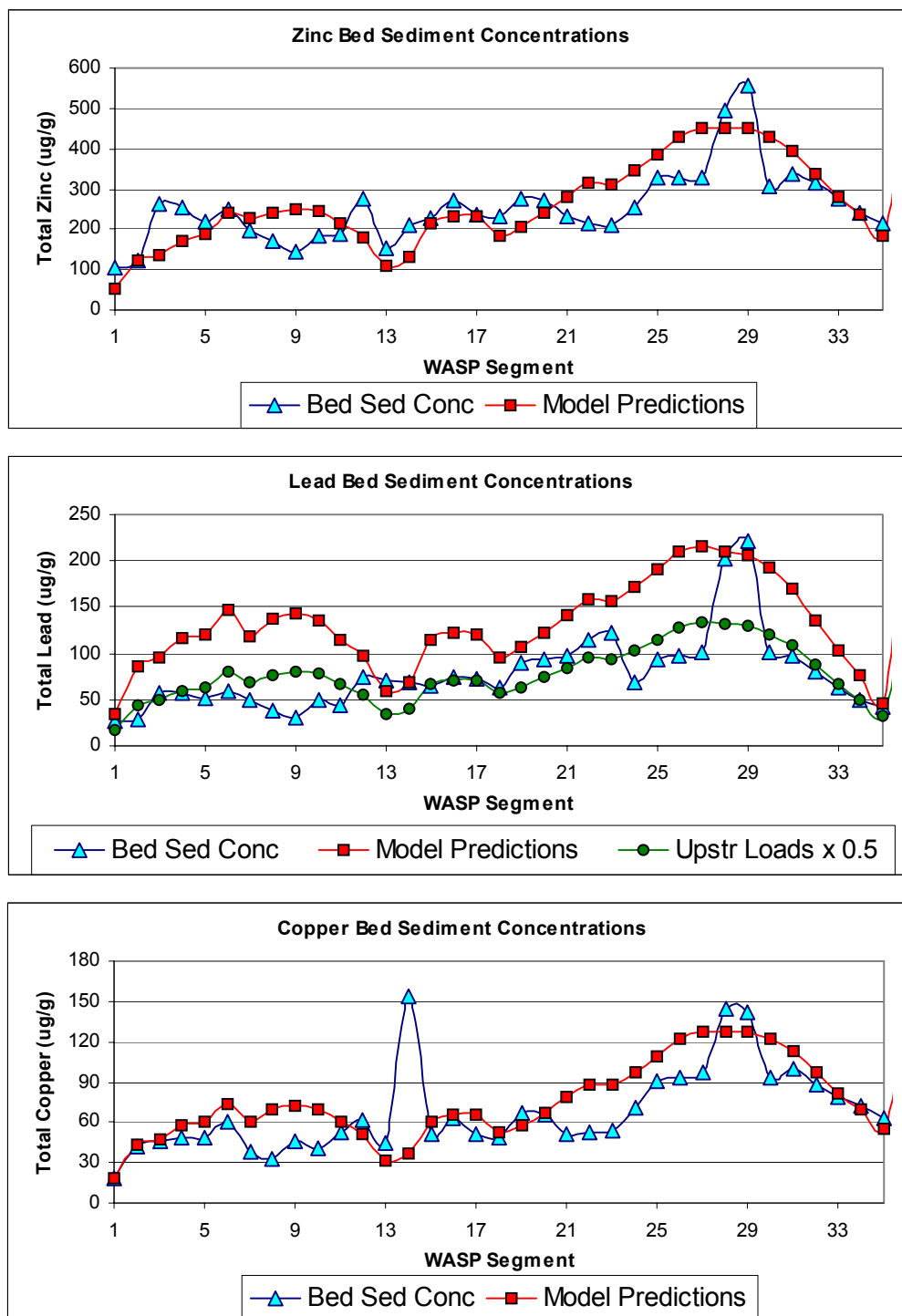


Figure 3-15. Metals Bed Sediment Results: Model Predictions for Last Day of 6-Year Run

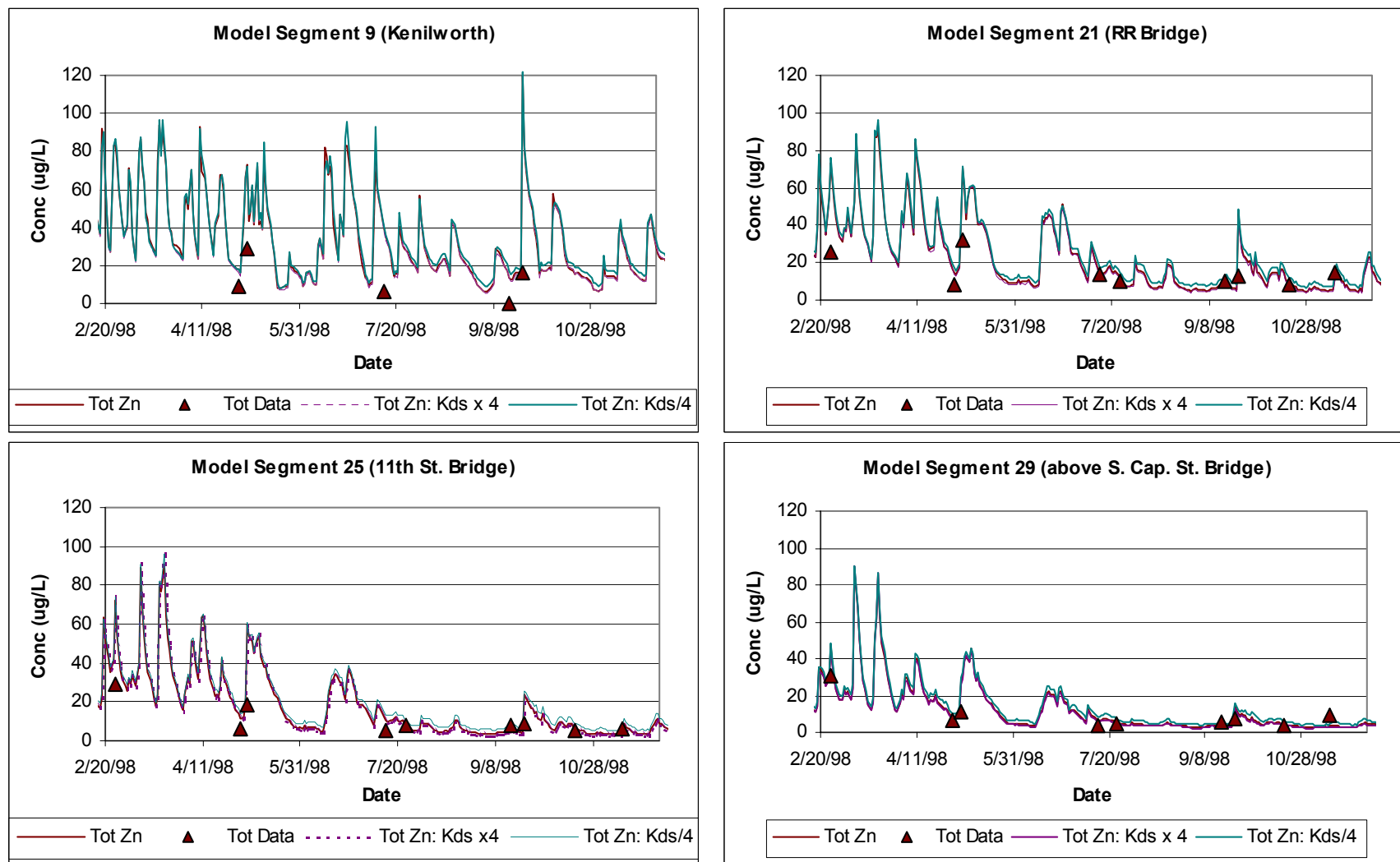


Figure 3-16. Zinc Water Column Results, Total Zinc: Calibrated Model and Kd Sensitivity Tests

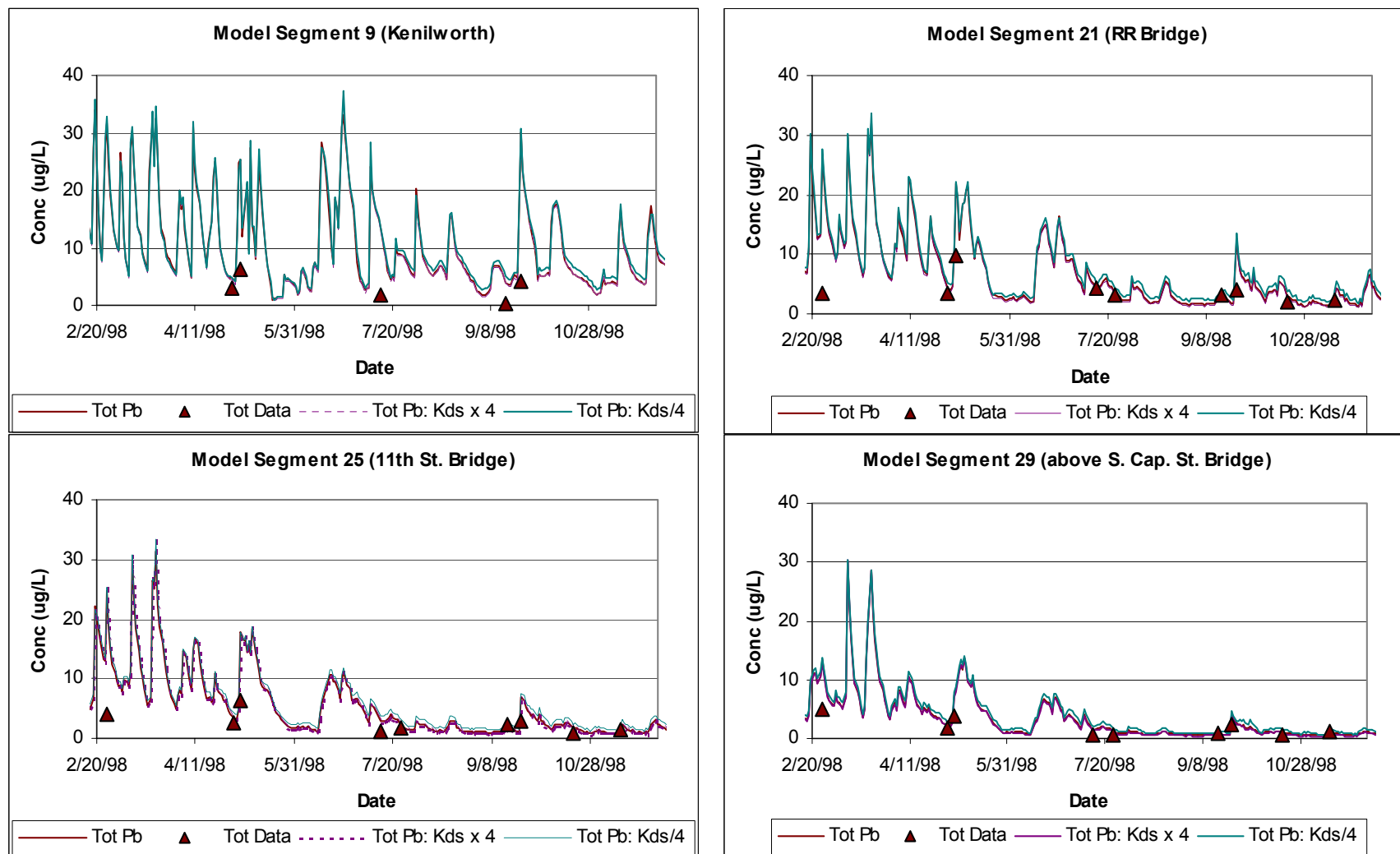


Figure 3-17. Lead Water Column Results, Total Lead, Using Upstream Load Factor of 0.5 Reduction: Calibrated Model and Kd

Sensitivity Tests

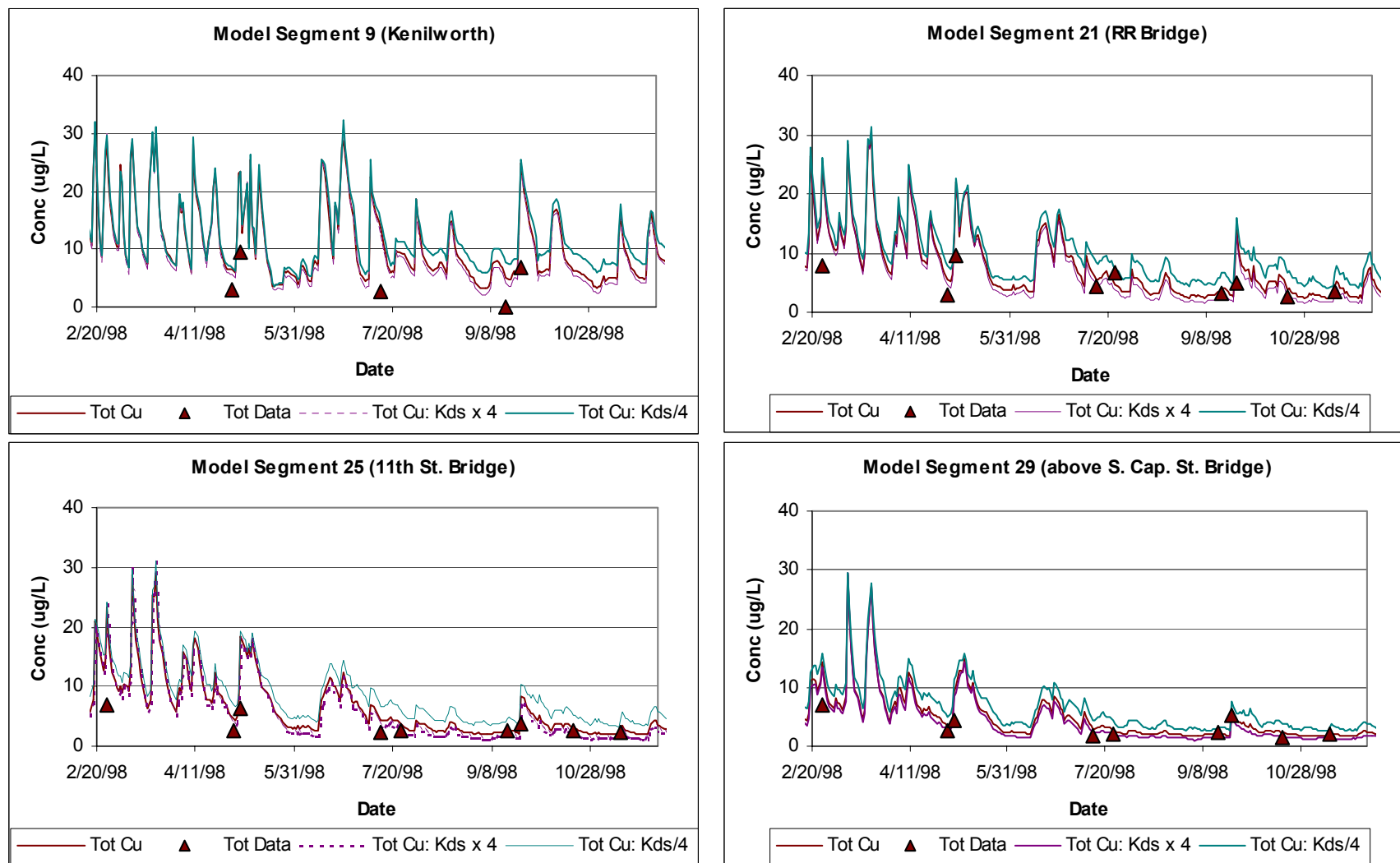


Figure 3-18. Copper Water Column Results, Total Copper: Calibrated Model and Kd Sensitivity Tests

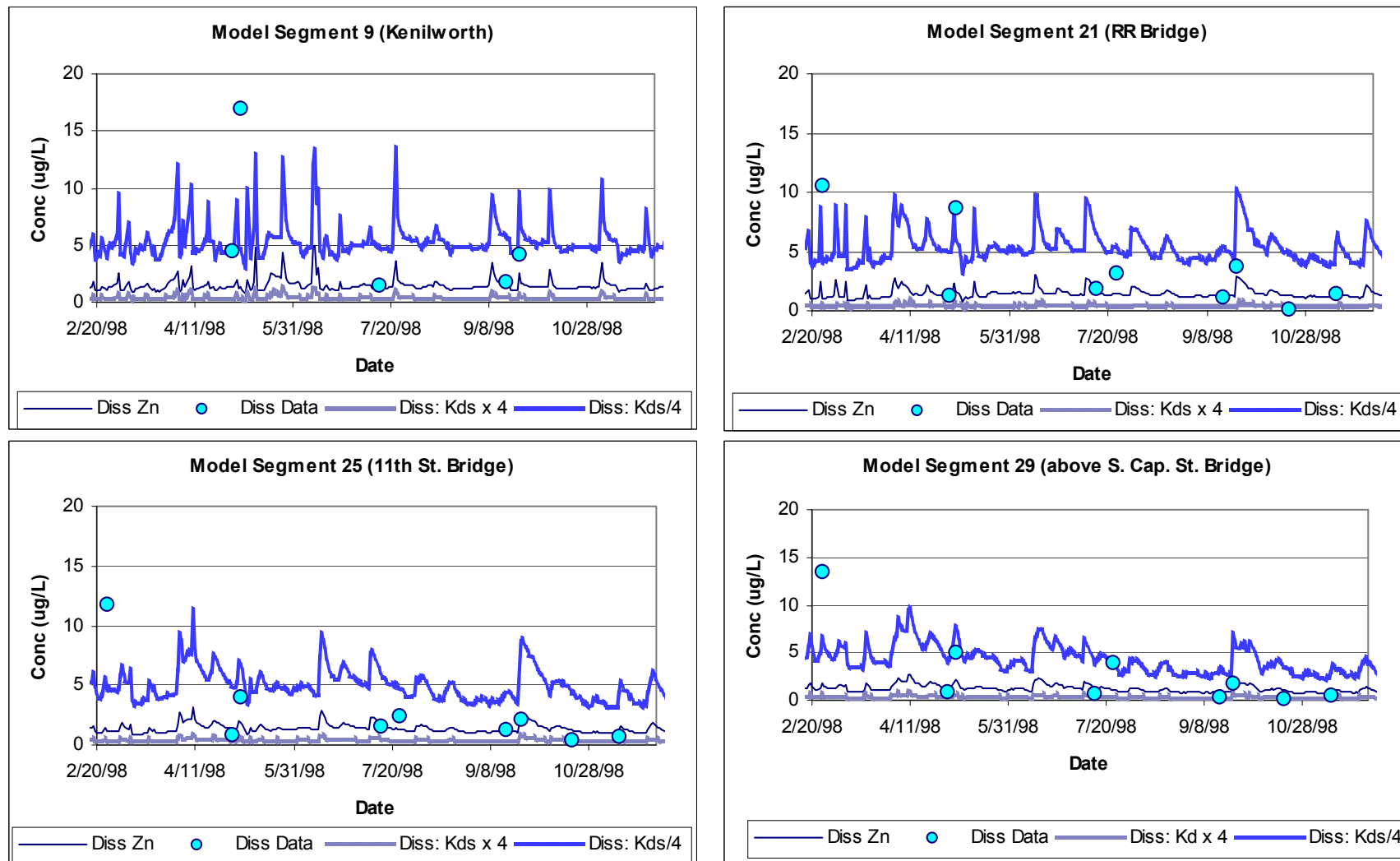


Figure 3-19. Zinc Water Column Results, Dissolved Zinc: Calibrated Model and Kd Sensitivity Tests

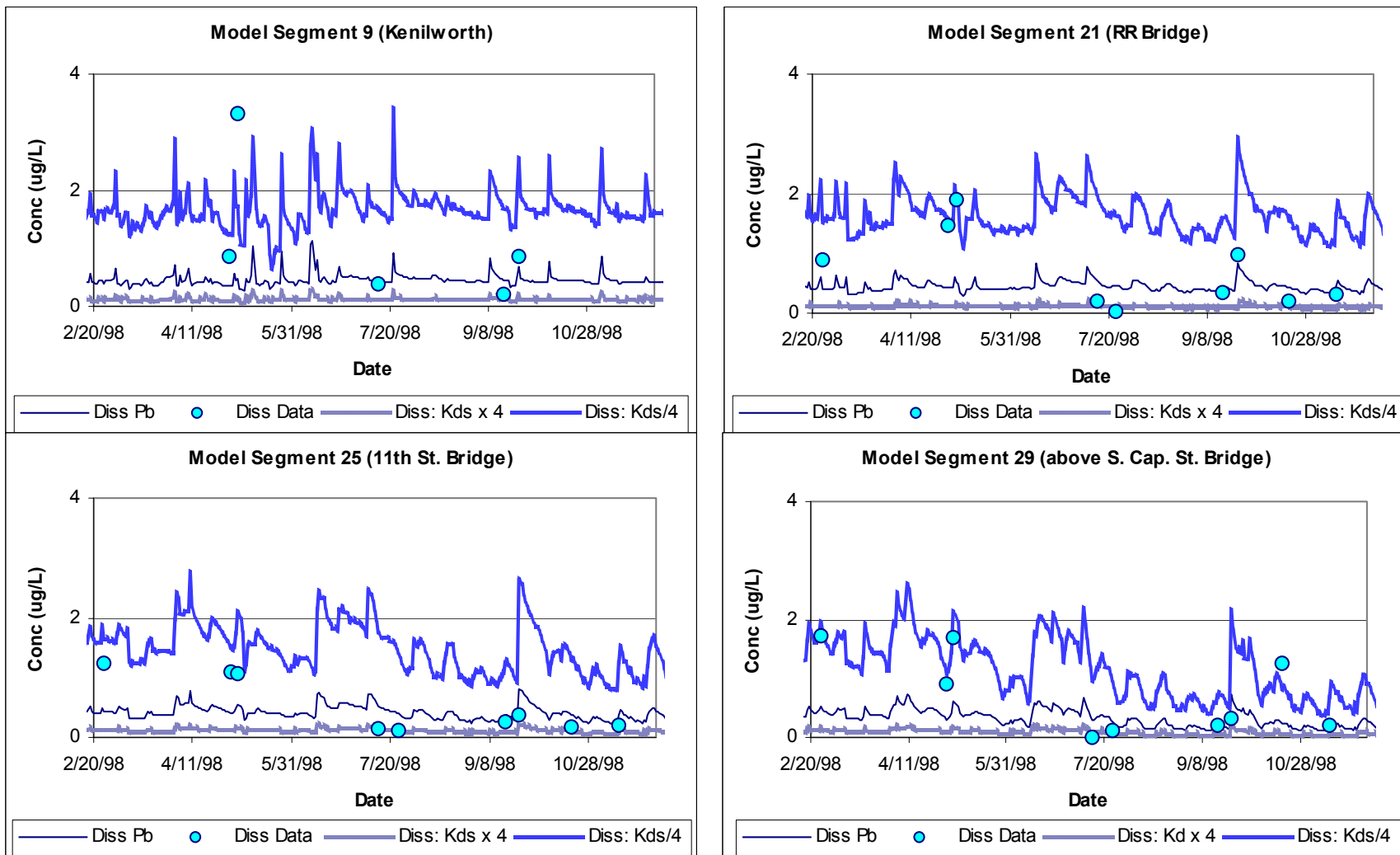


Figure 3-20. Lead Water Column Results, Dissolved Lead, Using Upstream Load Factor of 0.5: Calibrated Model and Kd

Sensitivity Tests

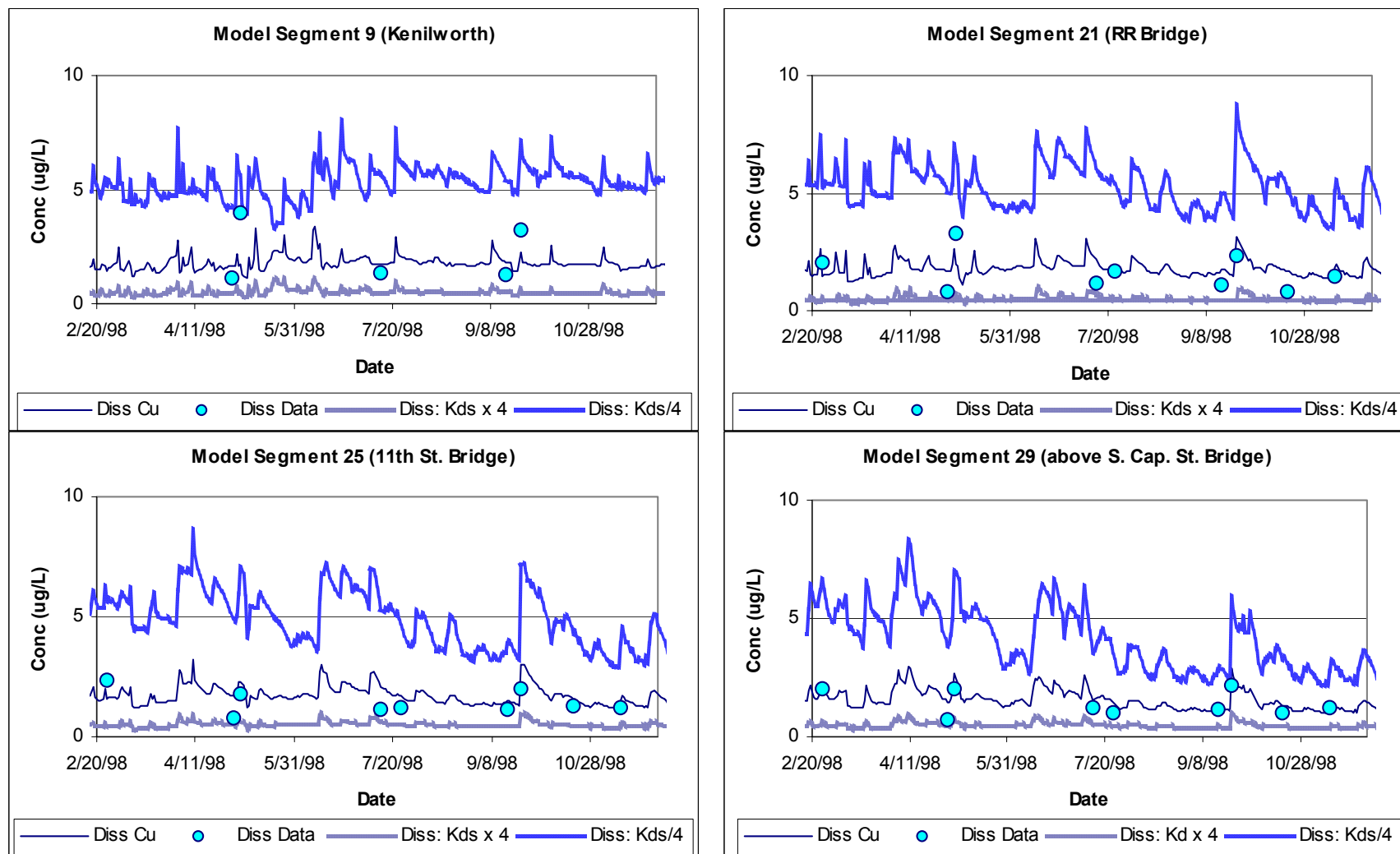


Figure 3-21. Copper Water Column Results, Dissolved Copper: Calibrated Model and Kd Sensitivity Tests

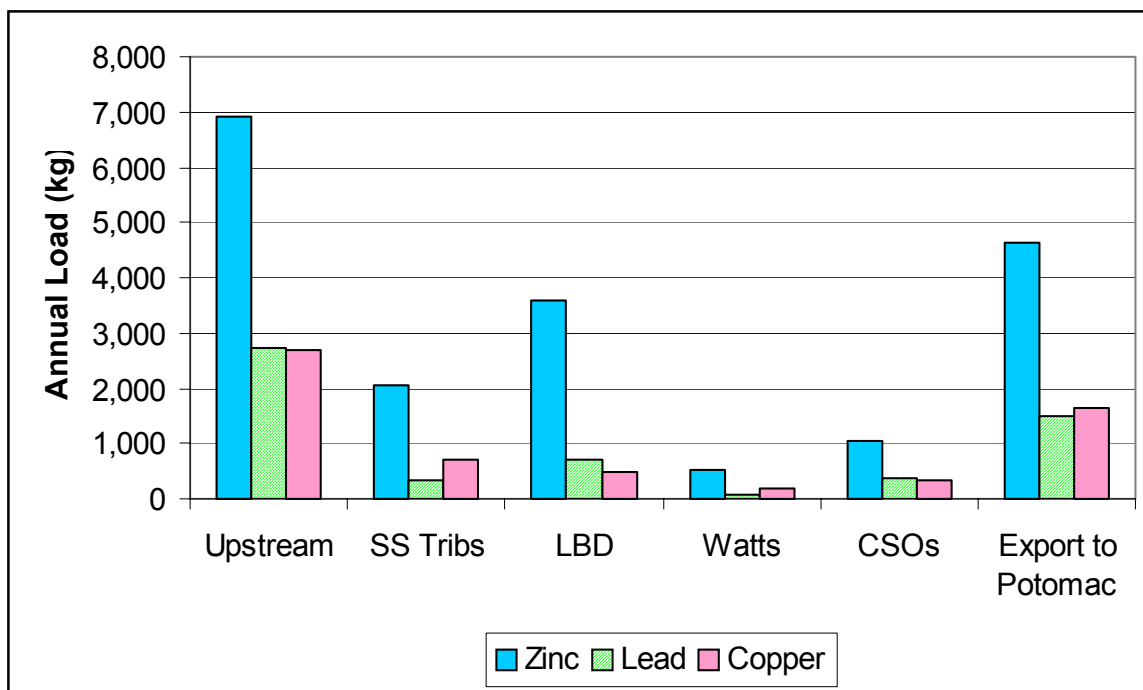


Figure 3-22. Summary of Average Annual Loads and Losses for the Calibrated Metals1 Sub-Model

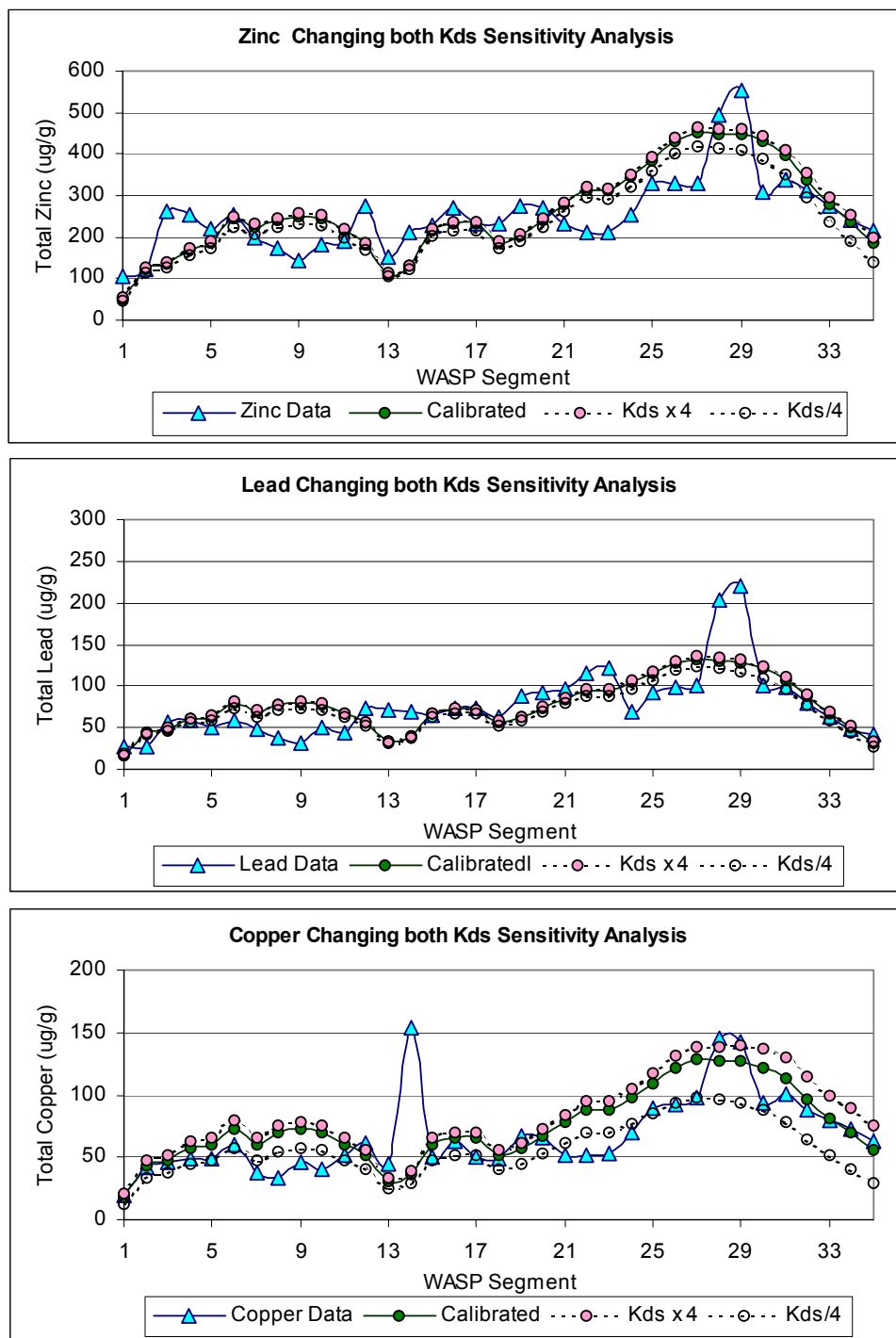


Figure 3-23. Metals Bed Sediment Results: Both Kds x 4; x 1/4

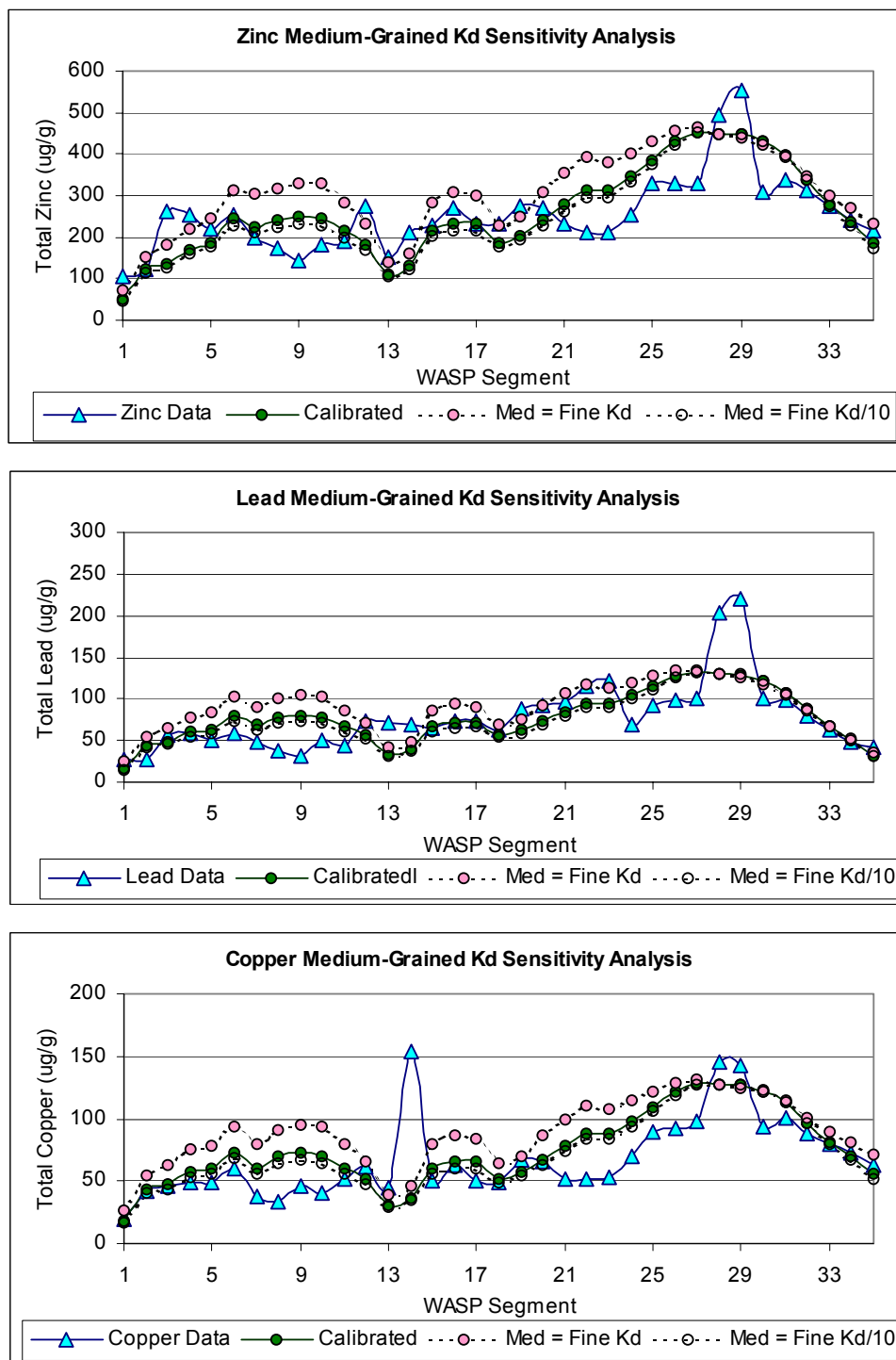


Figure 3-24. Metals Bed Sediment Results - K_d for med, 1/4, changed to 1 and to 1/10

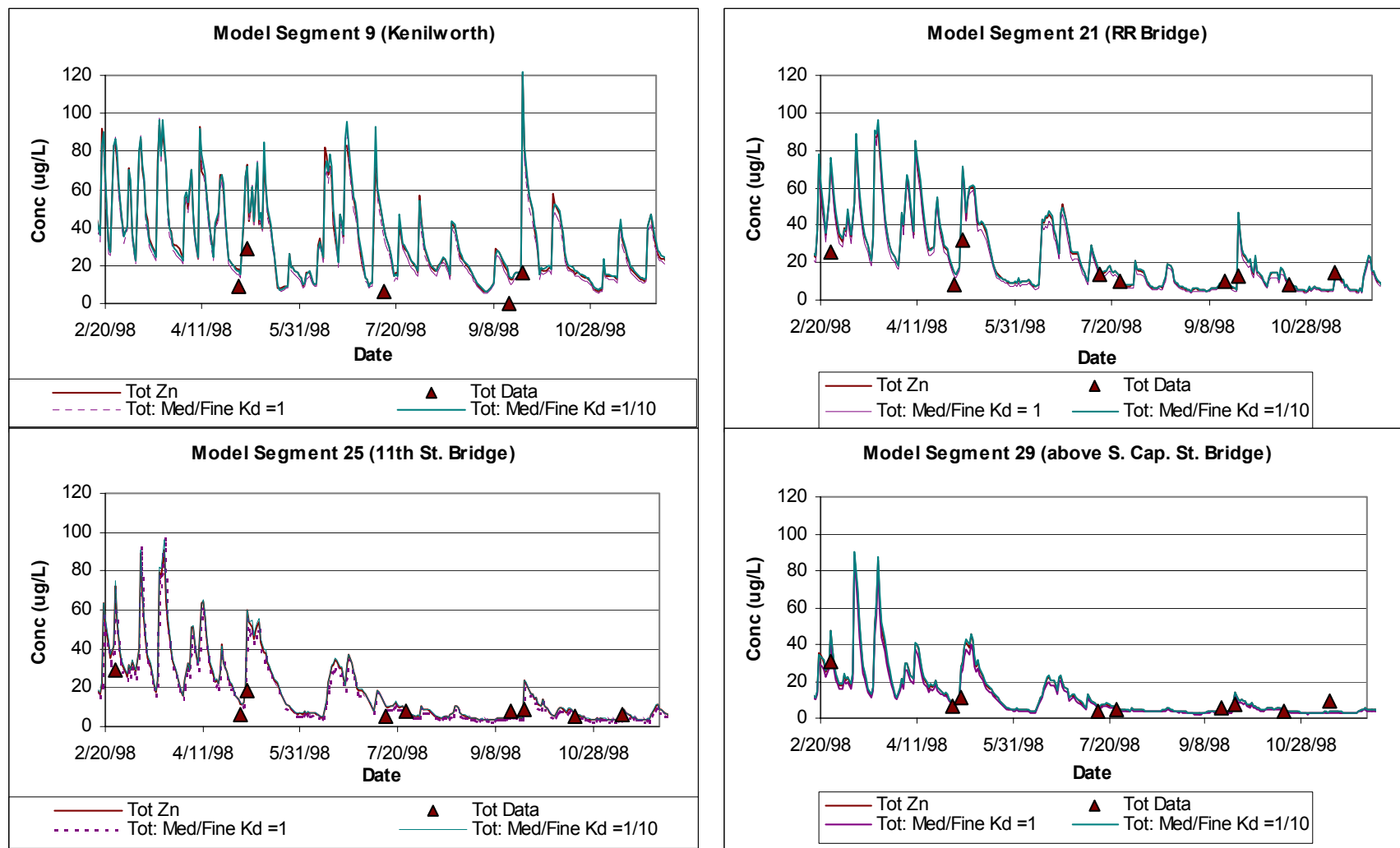


Figure 3-25. Zinc Water Column Results, Total Zinc: (K_d med)/(K_d fine) changed from 1/4 to 1 and to 1/10

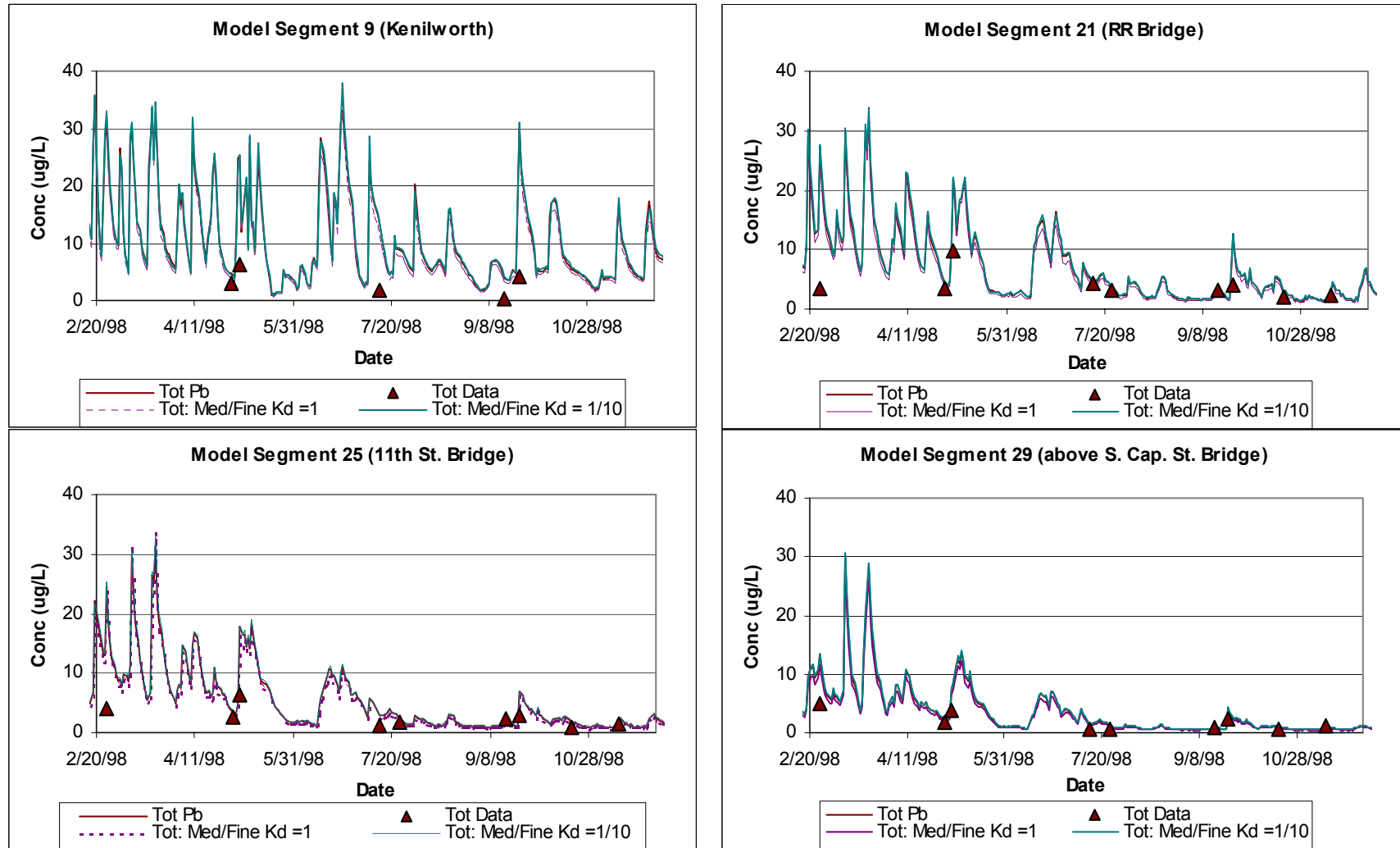


Figure 3-26. Lead Water Column Results, Total Lead: (K_d med)/(K_d fine) changed from 1/4 to 1 and to 1/10

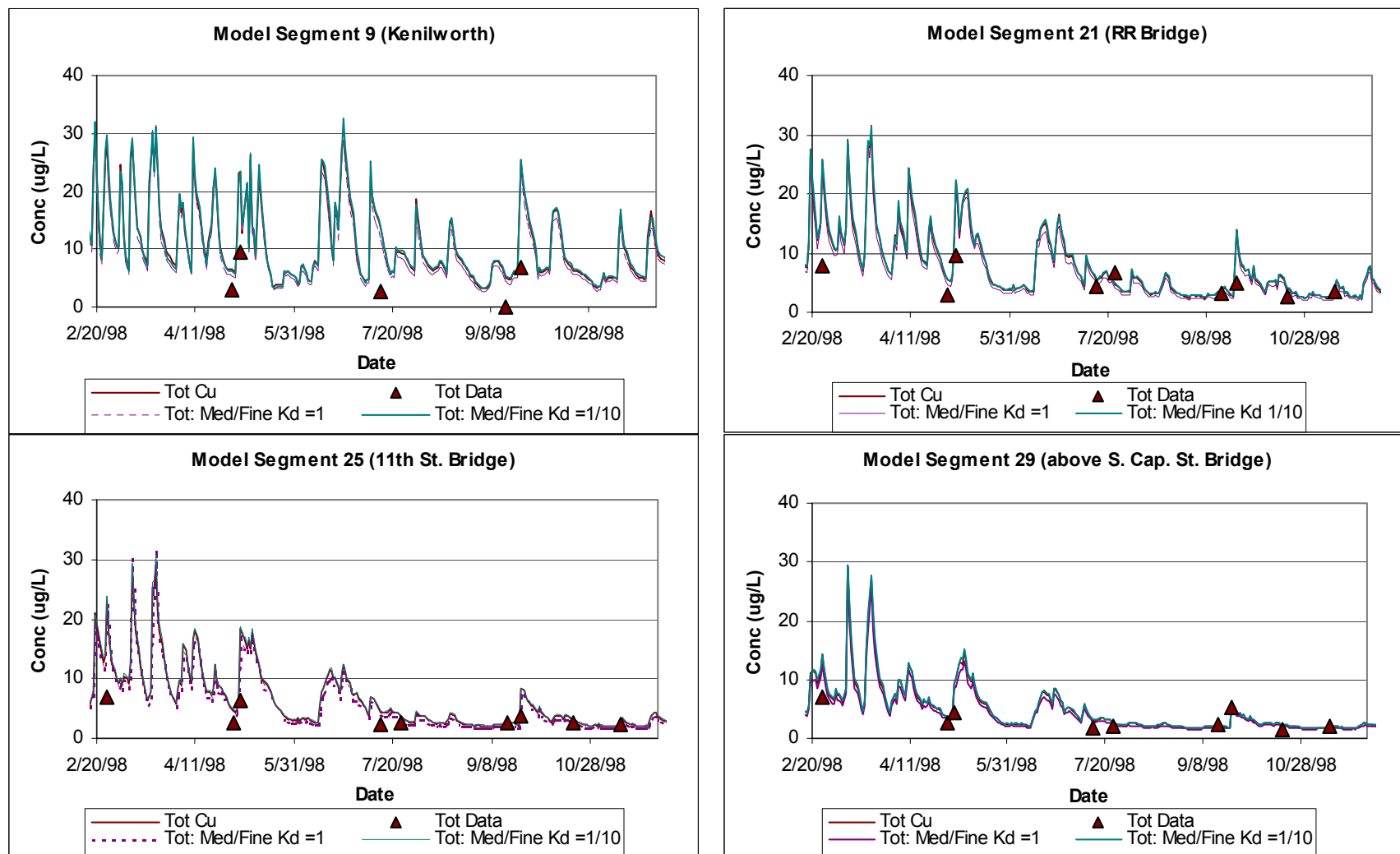


Figure 3-27. Copper Water Column Results, Total Copper: (K_d med)/(K_d fine) changed from 1/4 to 1 and to 1/10

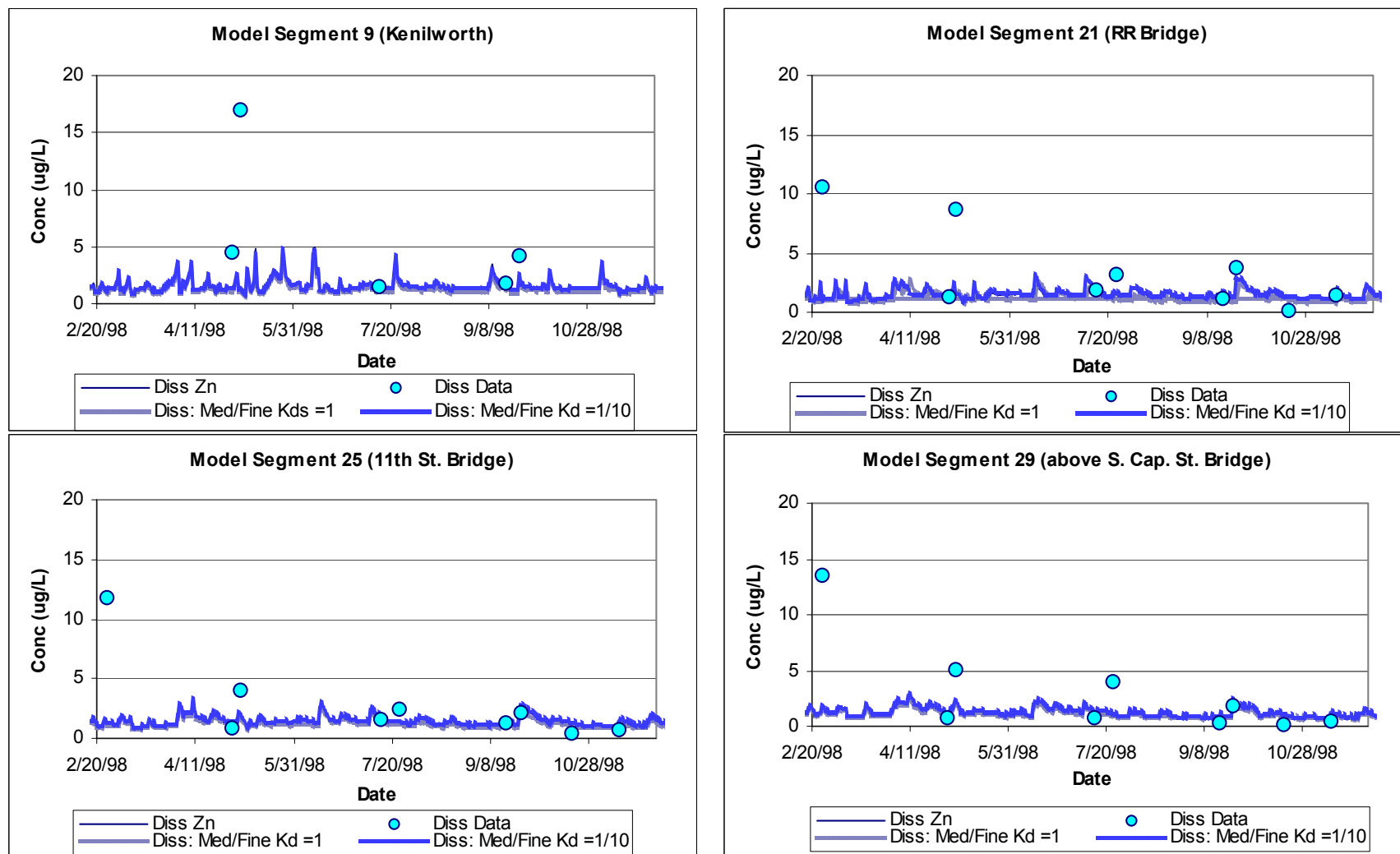


Figure 3-28. Zinc Water Column Results, Dissolved Zinc: K_d for med, 1/4, changed to 1 and to 1/10

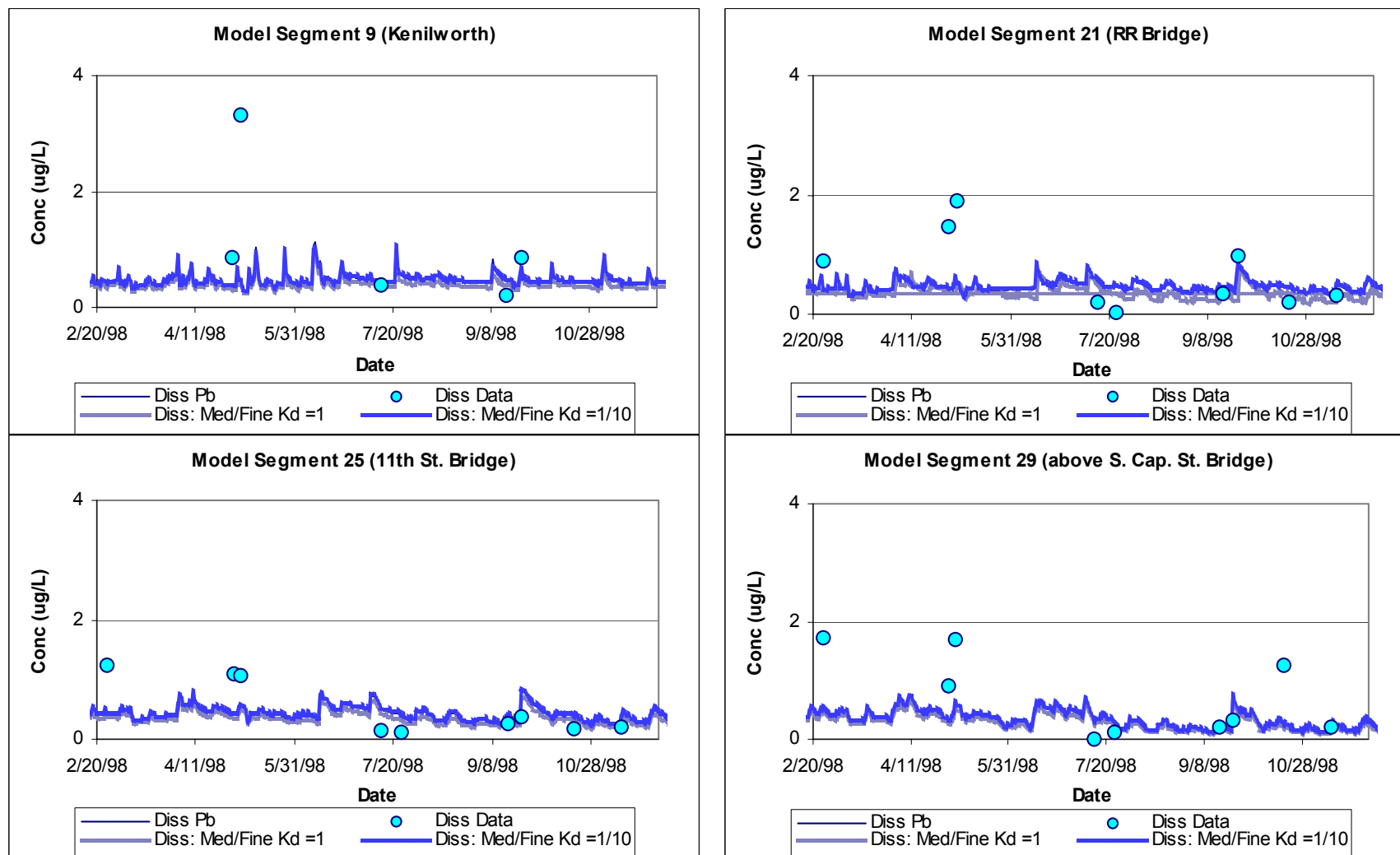


Figure 3-29. Lead Water Column Results, Dissolved Lead: K_d for med, 1/4, changed to 1 and to 1/10

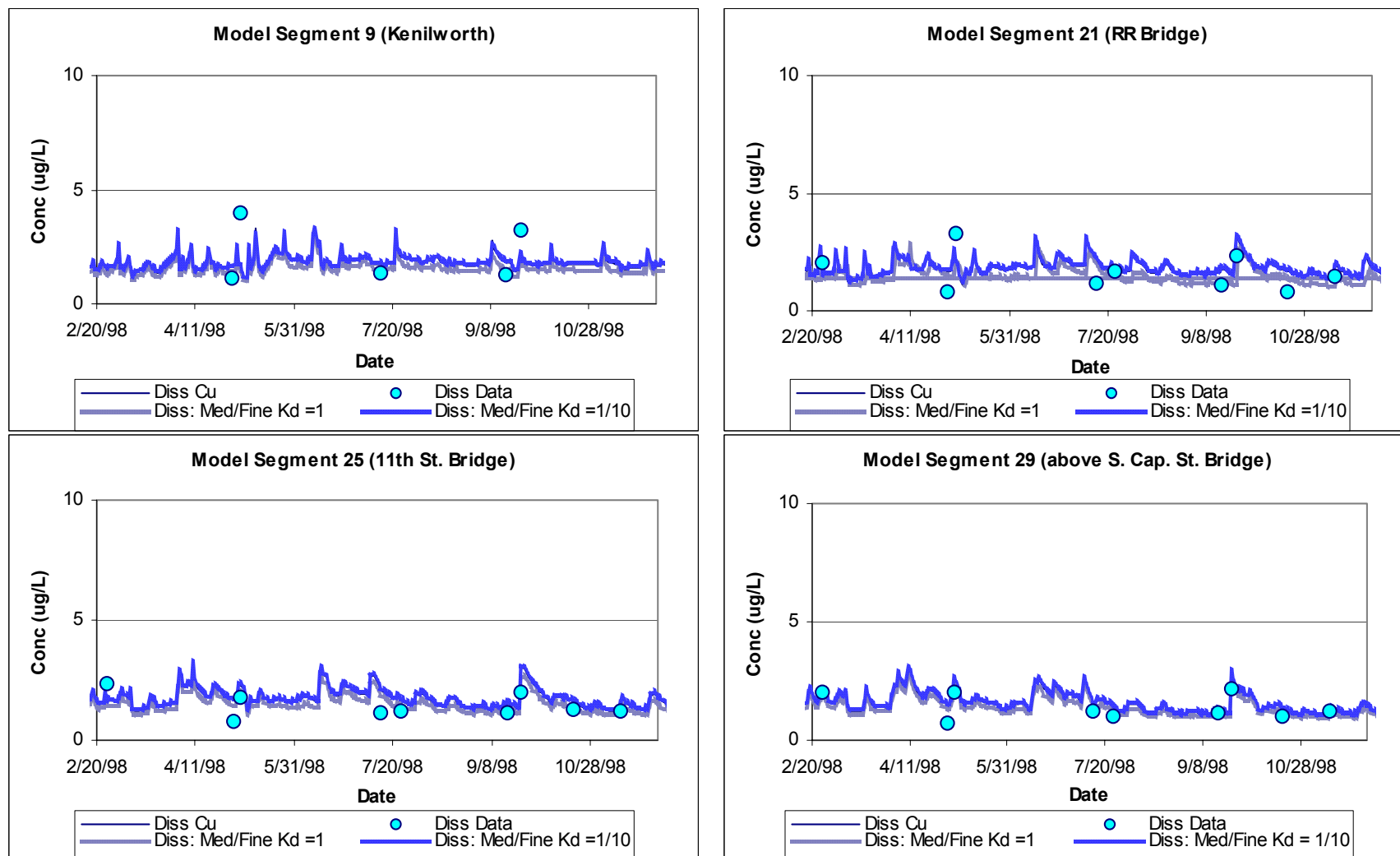


Figure 3-30. Copper Water Column Results, Dissolved Copper: K_d for med, 1/4, changed to 1 and to 1/10

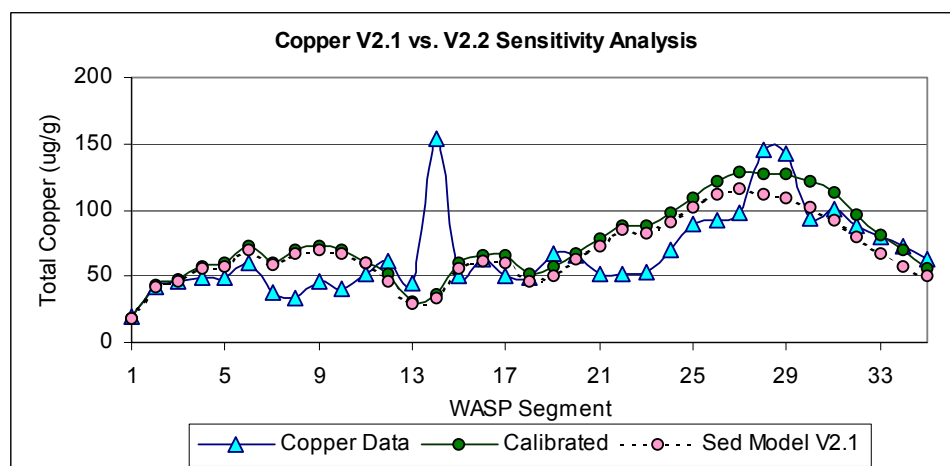
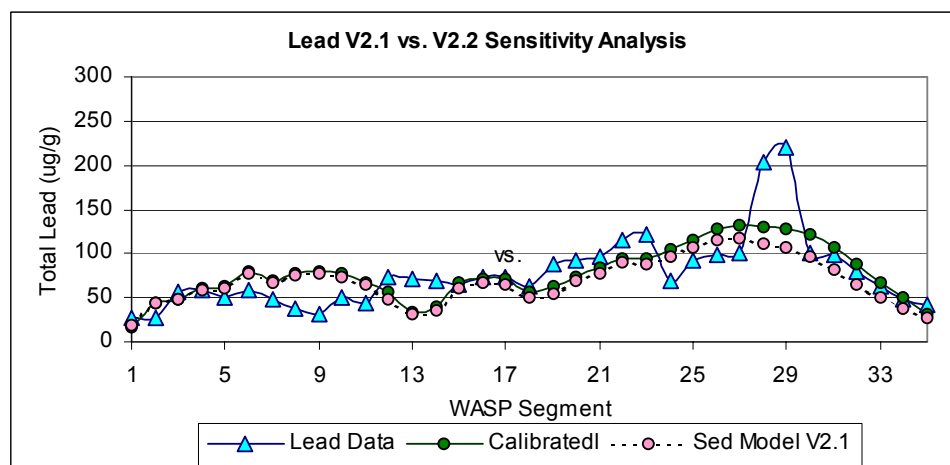
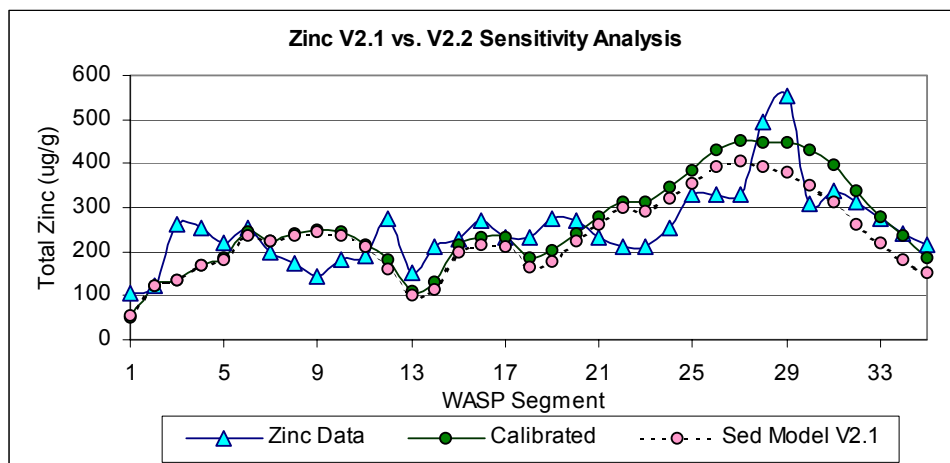


Figure 3-31. Metals Bed Sediment Results - Calibrated Model (Version 2.2) vs. Sediment Model (Version 2.1)

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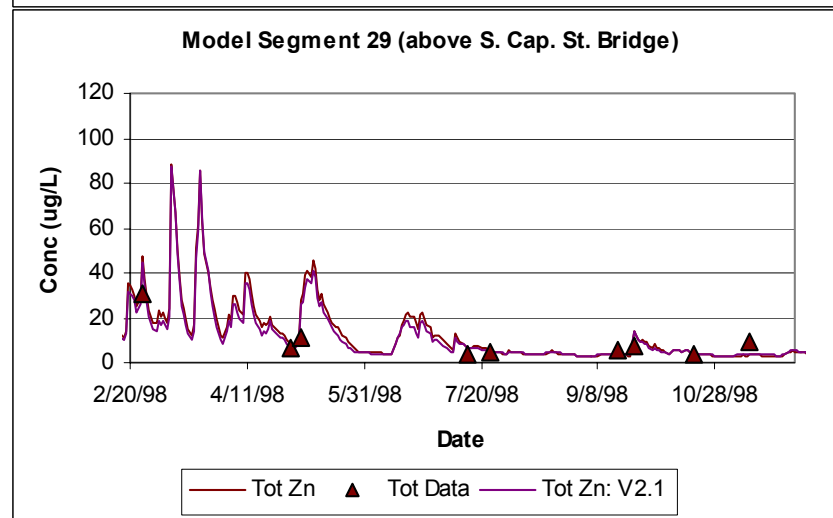
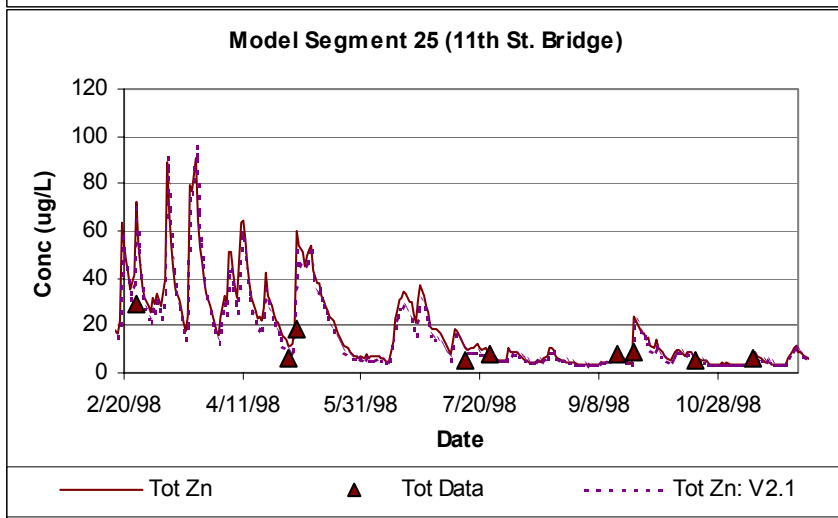
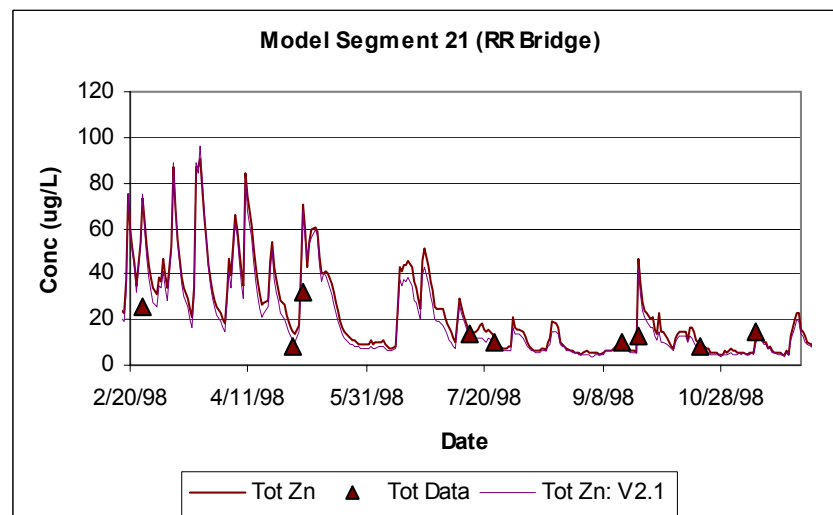
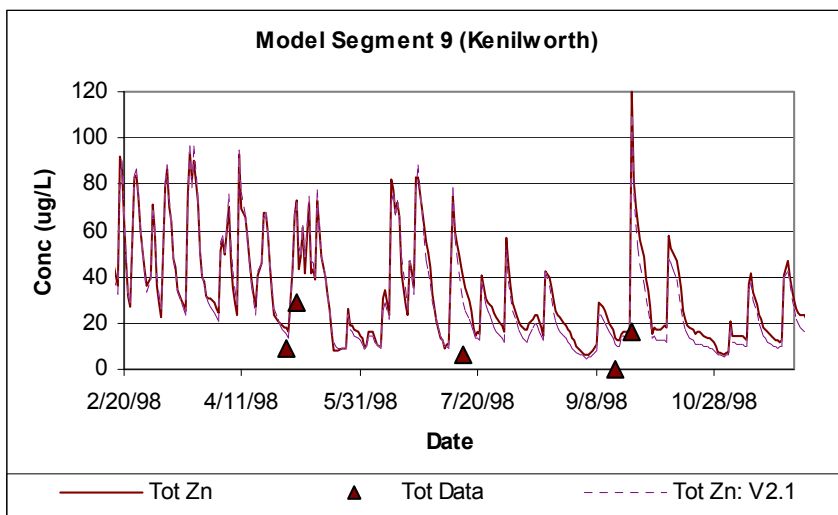


Figure 3-32. Zinc Water Column Results, Total Zinc: Calibrated Model (Version 2.2) vs. Sediment Model (Version 2.1)

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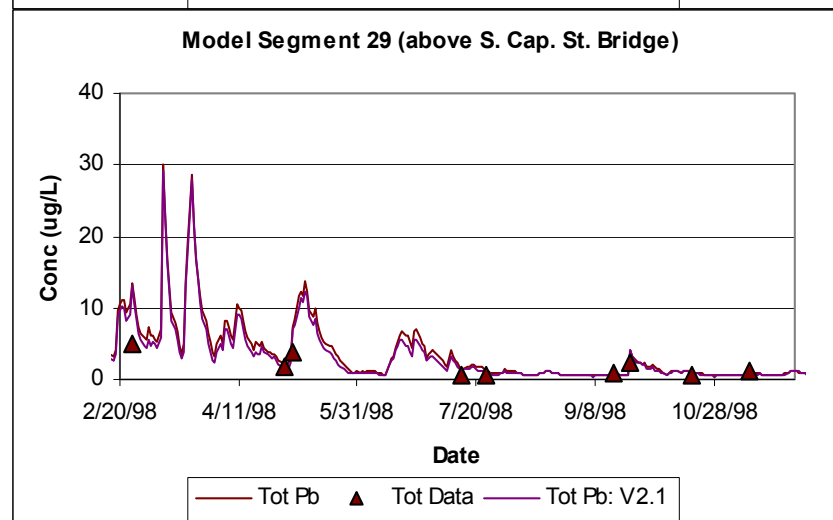
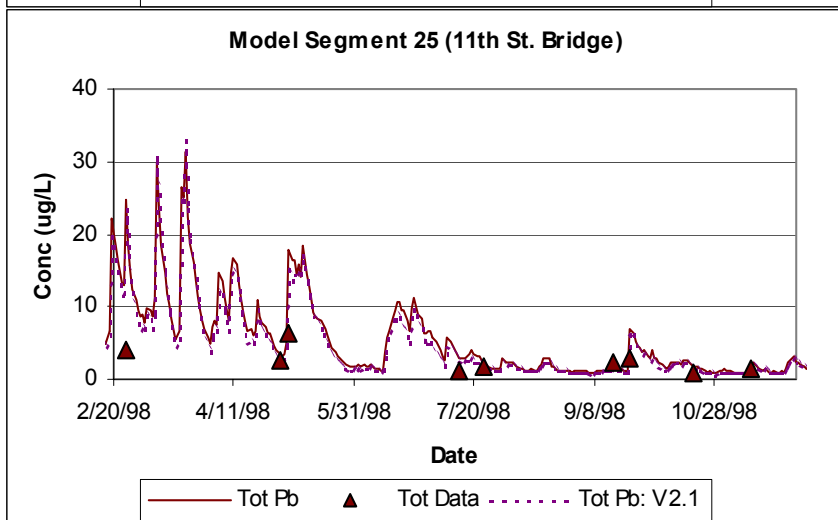
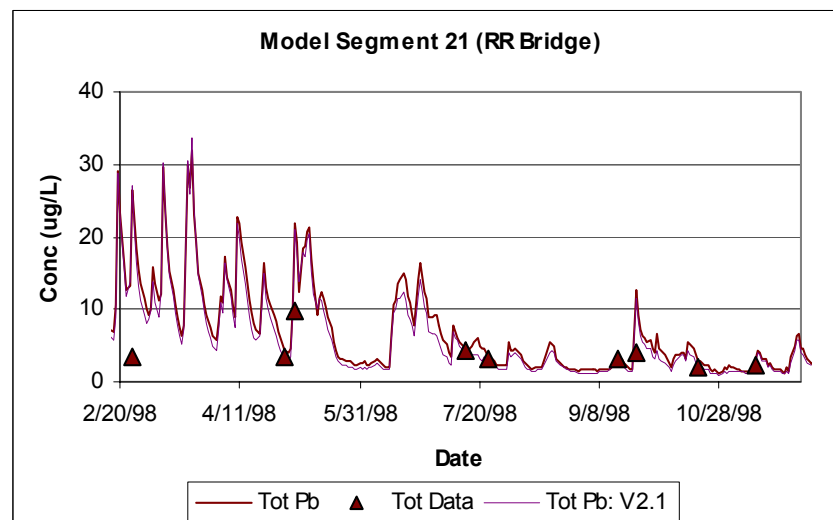
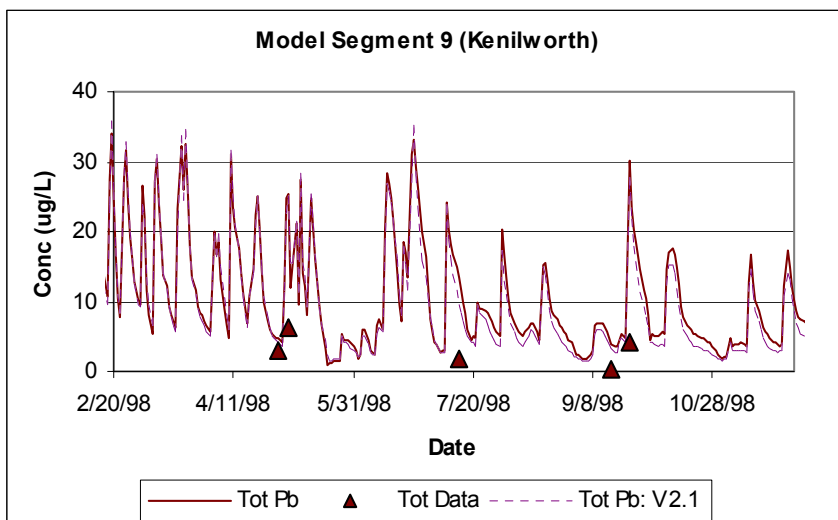


Figure 3-33. Lead Water Column Results, Total Lead: Calibrated Model (Version 2.2) vs. Sediment Model (Version 2.1)

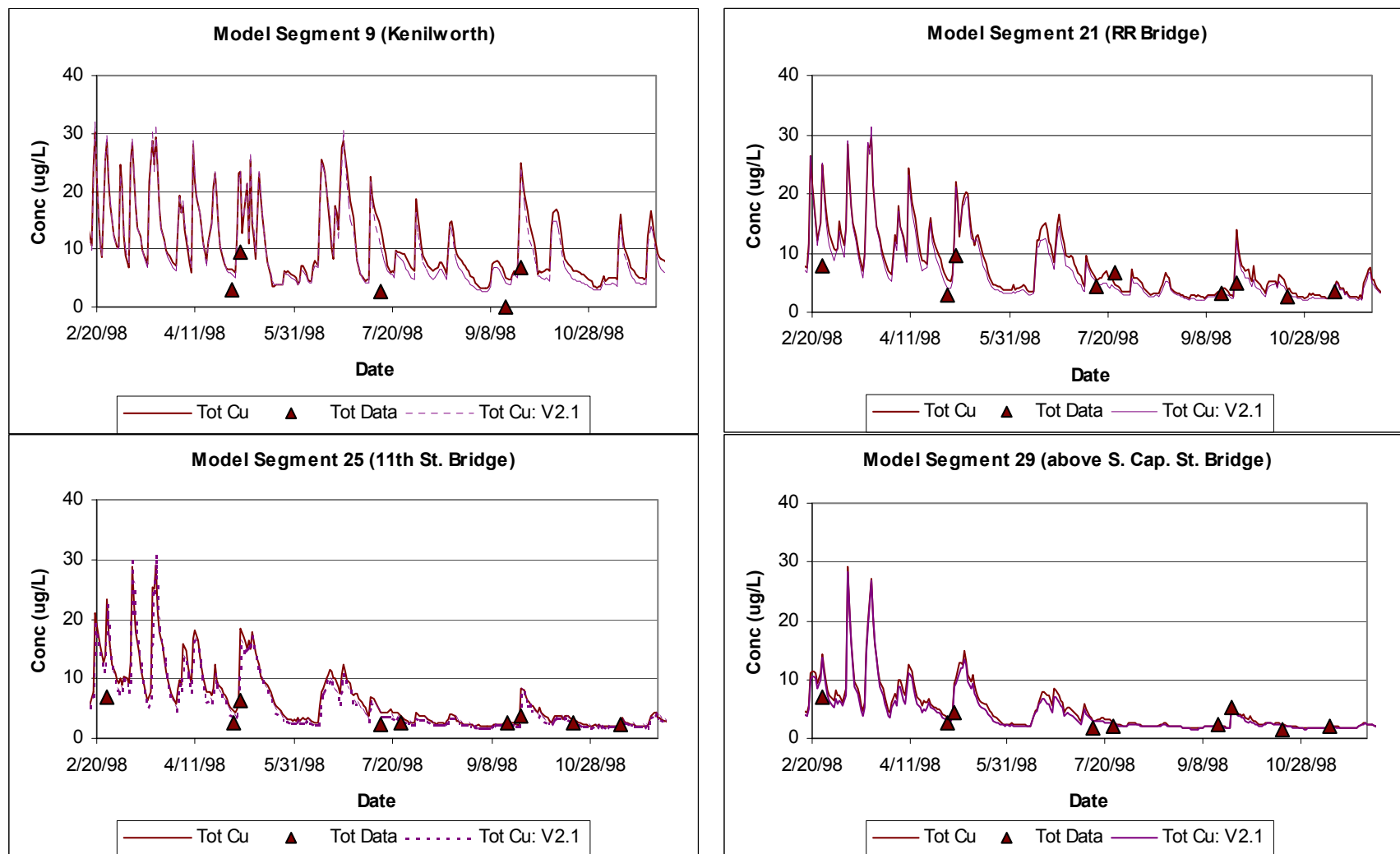


Figure 3-34. Copper Water Column Results, Total Copper: Calibrated Model (Version 2.2) vs. Sediment Model (Version 2.1)

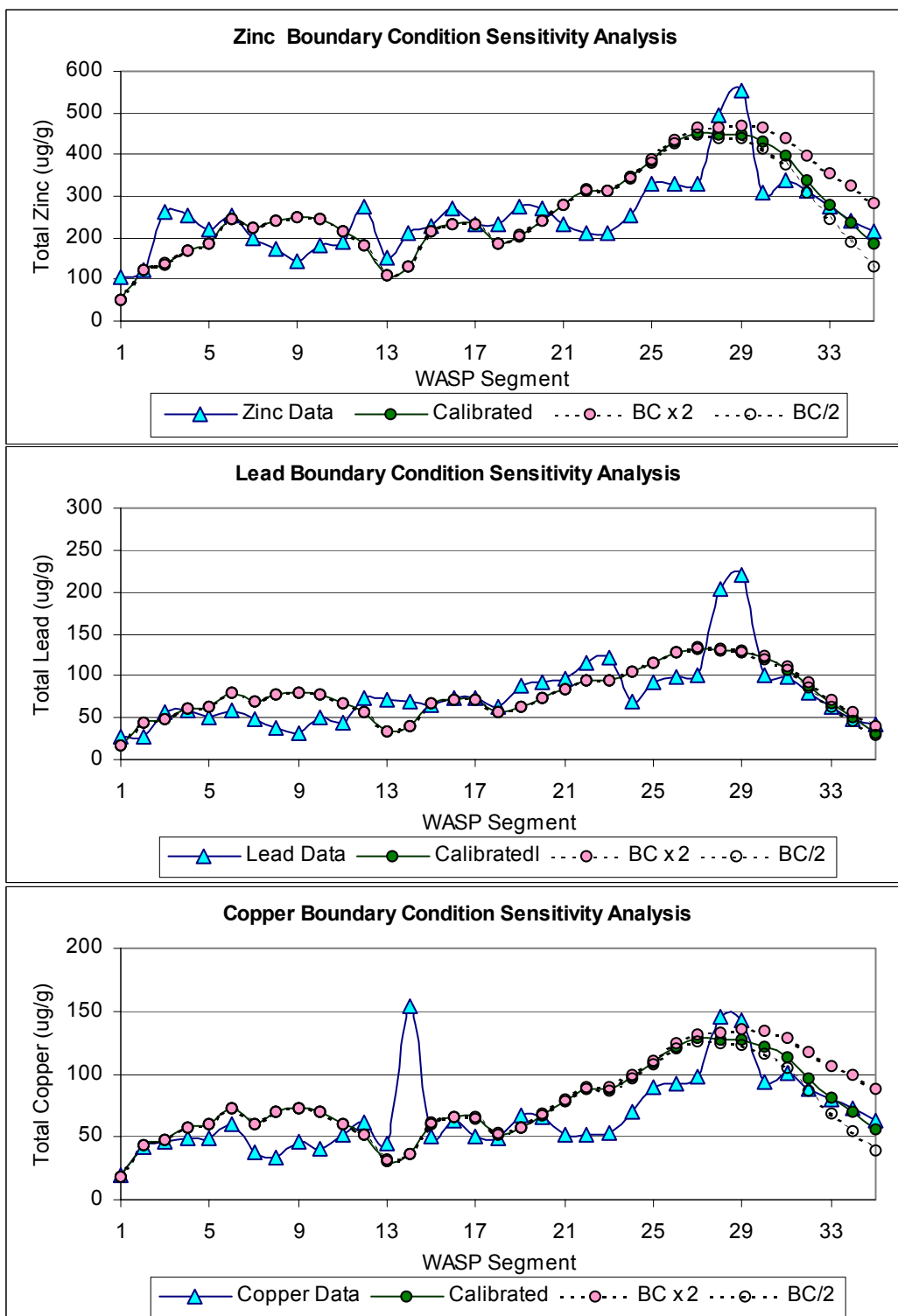


Figure 3-35. Metals Bed Sediment Results: Potomac Boundary Conditions x 2; x ½

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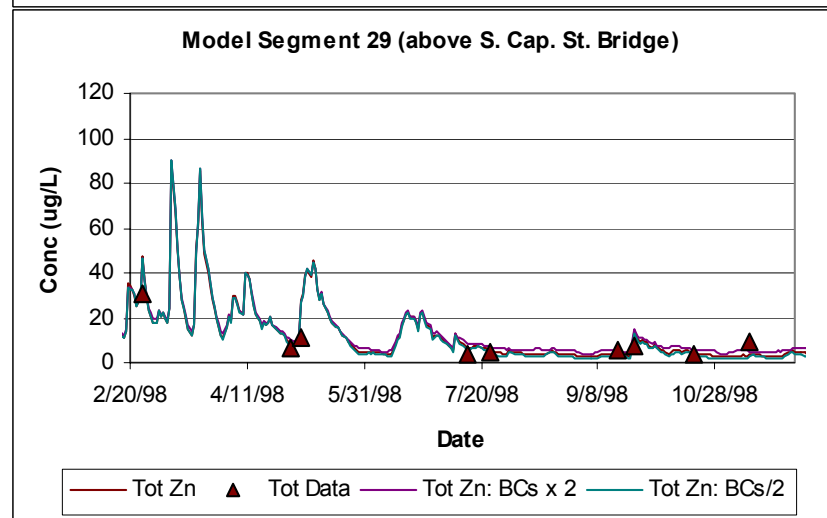
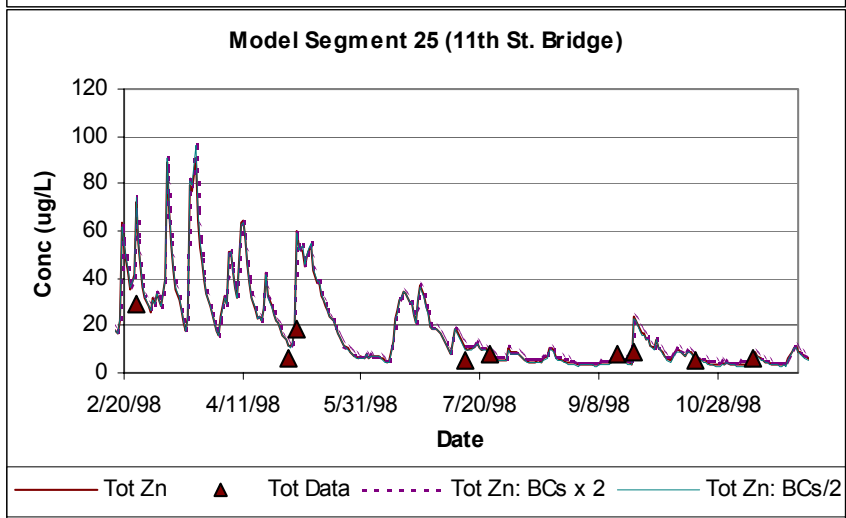
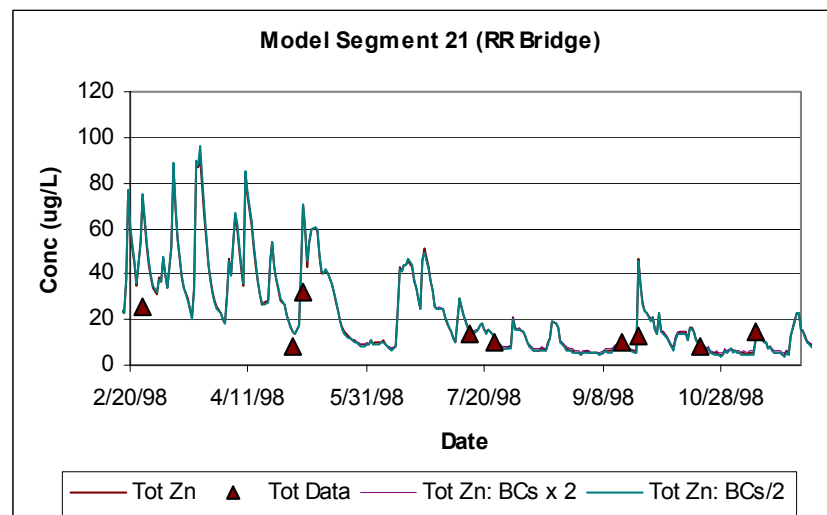
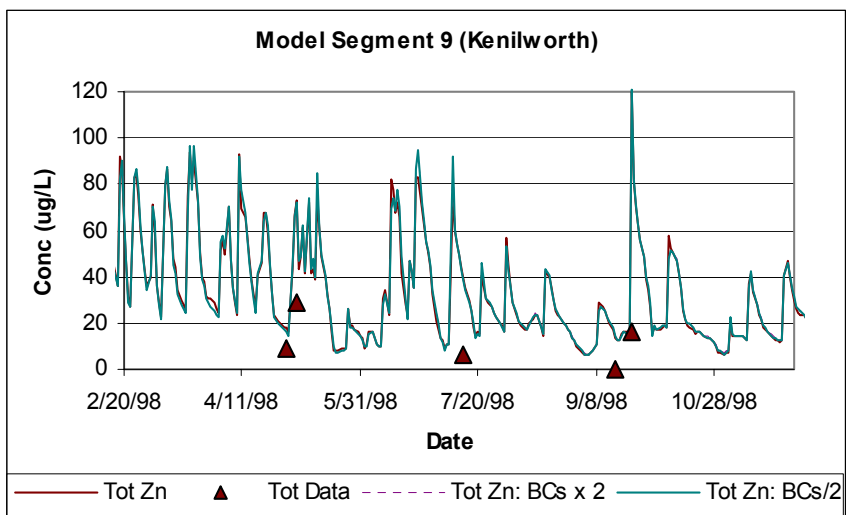


Figure 3-36. Zinc Water Column Results, Total Zinc: Potomac Boundary Conditions x 2; x ½

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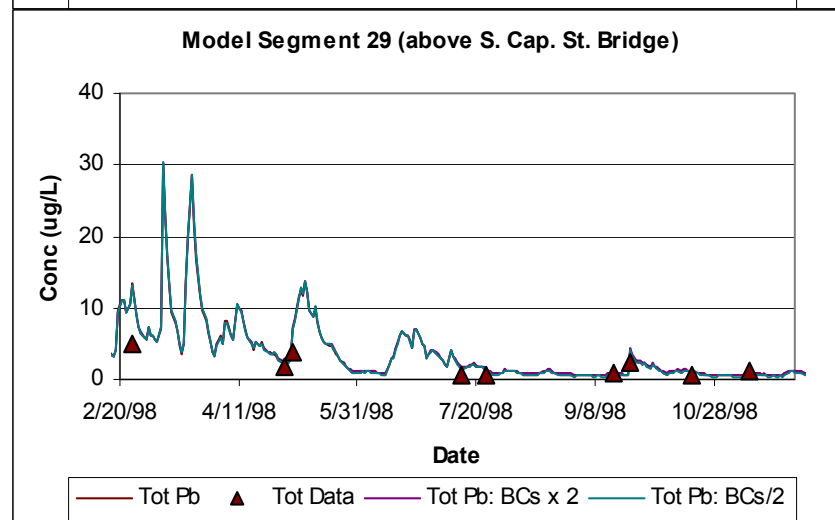
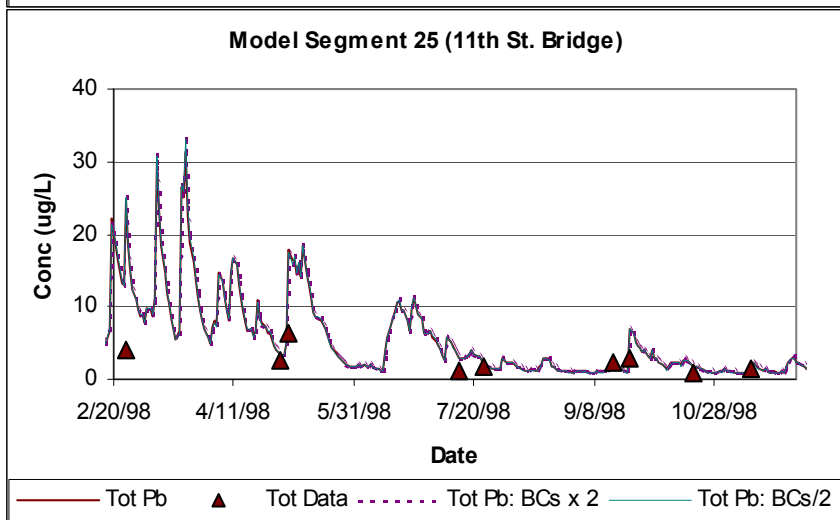
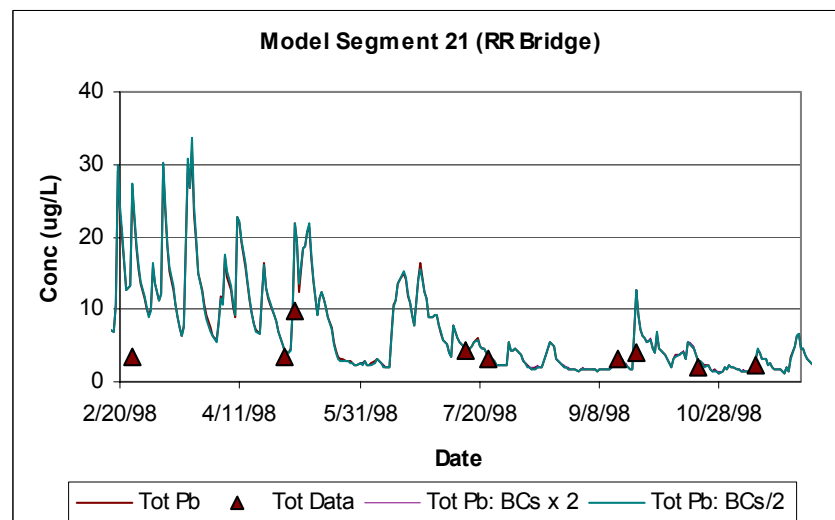
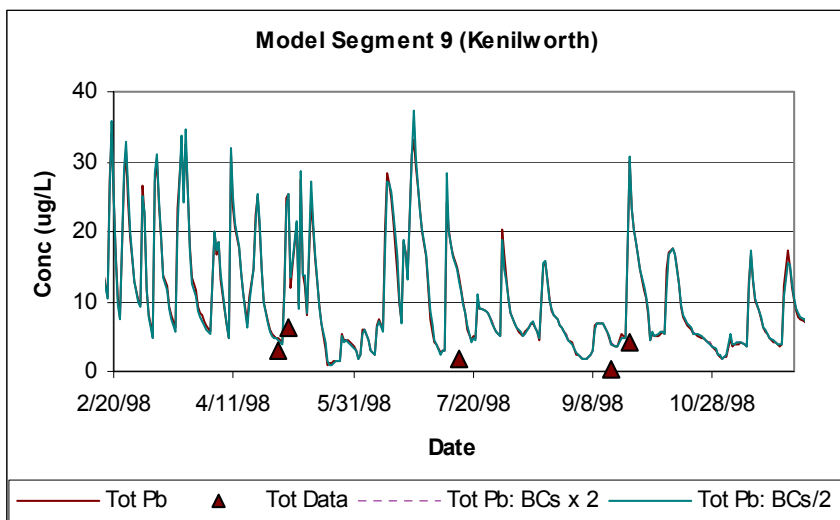


Figure 3-37. Lead Water Column Results, Total Lead: Potomac Boundary Conditions x 2; x ½

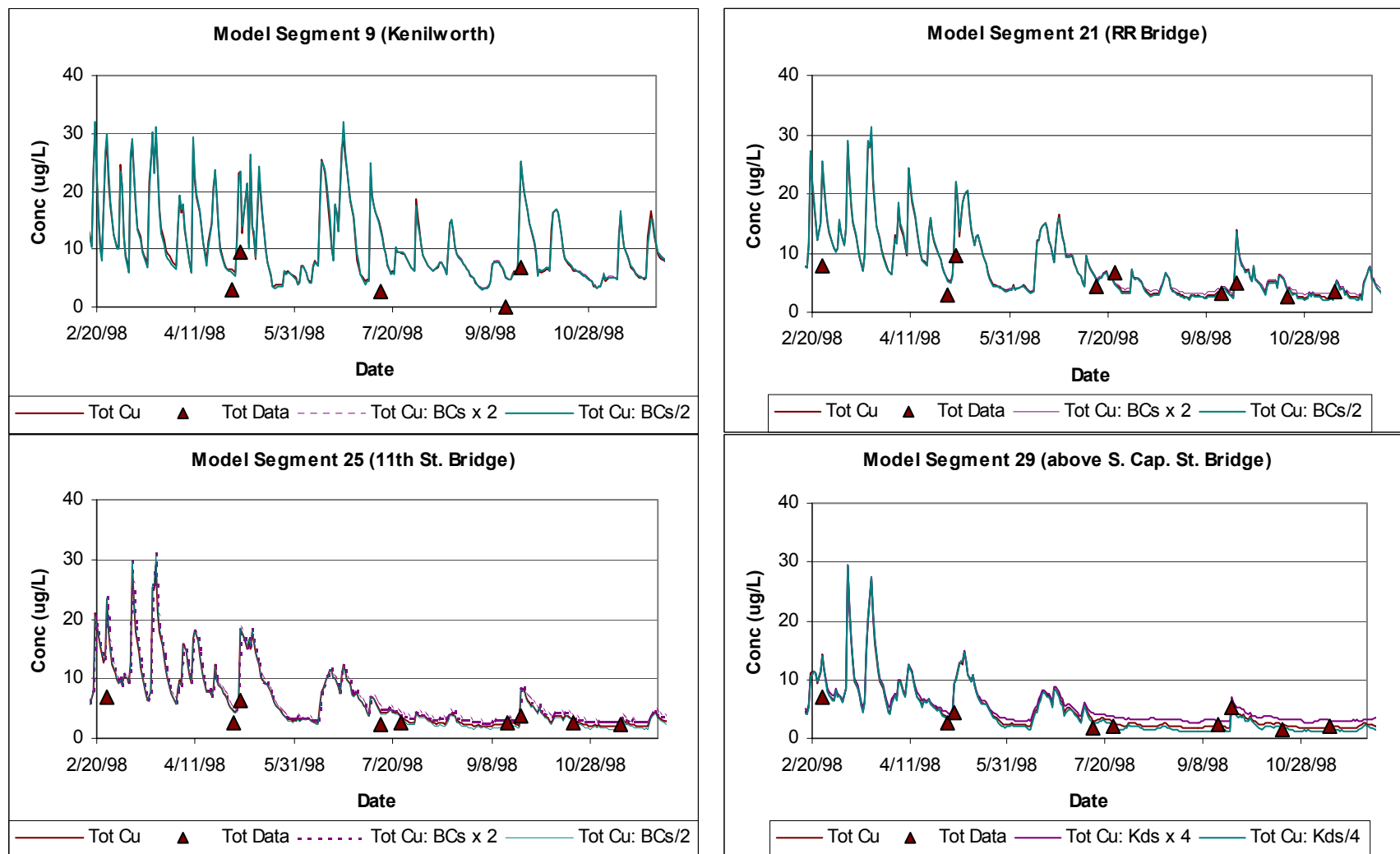


Figure 3-38. Copper Water Column Results, Total Copper: Potomac Boundary Conditions x 2; x 1/2

3.3.2. Metals2 (Arsenic) Sub-Model

Model Description

A very simple model has been set up for total arsenic, with no speciation. The only fate and transport process simulated, in addition to advection and dispersion, is absorption to the medium and fine-grained sediment fractions. ICPRB feels that this simple modeling framework is appropriate, given that data support for the arsenic model is limited. There is no data on arsenic in the Gruessner study of upstream loads (Gruessner et al., 1998), there is no arsenic data in the bed sediment study by Velinsky et al. (2001), and there is no data to compute site-specific distribution coefficients. However, though data support is limited, the existing data exhibits little variability in either the water column or bed sediment.

Input Parameters

Upstream baseflow concentrations are estimated at 0.2 ug/L, from a limited amount of data available in the water column sampling done by Velinsky in 1998 (Velinsky et al., 1999), which included two baseflow arsenic concentrations for both the NE and NW branches. Tidal sub-basin tributaries and separate storm sewer (SS) system arsenic concentrations are all estimated at 1.4 ug/L, based on currently available MS4 monitoring data (20 samples with 15 non-detects, where non-detects were estimated to be ½ the detection limit). Bed sediment arsenic concentrations can be estimated from several historical data sets available in the AWT/NOAA database (though coverage is limited, with most samples near the west bank of the river directly adjacent to the Washington Navy Yard or the Washington Gas and Light facility, no samples below the S. Capitol Street Bridge and only a few samples above the Railroad Lift Bridge.) Tidal sub-basin tributary baseflow and groundwater concentrations are estimated to be 0.2 ug/L, based on the NE/NW Branches baseflow results. NE/NW Branches stormflow concentrations and combined sewer system overflows (CSOs) concentrations are estimated to be 1.4 ug/L, based on the MS4 monitoring results.

Because no site-specific data was available to estimate partition coefficients for arsenic, literature values were used. Diamond et al. (1990; 1995) computed arsenic K_d 's of 30,000 - 60,000 and 150,000 L/kg using water column data from two Canadian lakes. A value of $K_d = 100,000$ L/kg was used in the arsenic model. A boundary condition for arsenic concentration at the Potomac confluence was set at 0.35 ug/L, equal to the mean of two pre-storm Potomac River concentrations reported in the Velinsky 1998 water column data set.

Model Results

A comparison of model predictions (last day of 6 year run) versus empirical bed sediment concentration data suggests that the arsenic model accounts reasonably well for arsenic mass inputs into the tidal portion of the Anacostia, though predicted bed sediment concentrations are about 20% too low. (It should be noted that empirical arsenic sediment concentrations for the first six and the last six model segments are just based on extrapolation because there were no samples located in these segments.) Likewise, predicted water column concentrations match the limited amount of available data reasonably well. Mass balance estimates for arsenic, given in Table 3-8 and Figure 3-25, should be viewed as very preliminary, because no actual concentration data was available for most of the sources listed (see comments in Table 3-7).

Table 3-6. WASP Input Parameters for Metals2 Sub-Model

Process	Parameter	Units	Arsenic	Source
<i>Adsorption:</i>				
	K _d for fine-grained sediment	L _w /kg _s	100,000	Based on literature values.
	K _d for coarse-grained sediment	L _w /kg _s	20,000	Based on literature values and best professional judgement.
<i>Downstream boundary condition:</i>				
	Typical Potomac concentration	ug/L	0.35	Computed from Velinsky et al. 1998 data from 2 pre-storm samples.
<i>Air/Water exchange:</i>				
	Wet deposition		0	No data has been found.
	Dry deposition		0	No data has been found.
	Volatilization input parameters		NA	Volatilization has not been included in the model.

Table 3-7. Concentrations Used to Compute Metals2 Sub-Model Calibration Run Input Loads (ug/L)

Source	Arsenic Orig	Suggested Arsenic Multiplier	Arsenic Final	Comment
NW Br Base	0.2	x 1	0.2	Concentration computed from Velinsky et al. 1998 data from 2 samples.
NW Br Storm	1.4	x 1	1.4	Assuming DC MS4 value.
NE Br Base	0.2	x 1	0.2	Concentration computed from Velinsky et al. 1998 data from 2 samples.
NE Br Storm	1.4	x 1	1.4	Assuming DC MS4 value.
SSTrib Base	0.2	x 1	0.2	Assuming Velinsky 1998 value.
SSTrib Storm	1.4	x 1	1.4	Concentration computed from available DC MS4 monitoring data, 20 samples with 15 NDs.
CSO	1.4	x 1	1.4	Assuming DC MS4 value.

Table 3-8. Average Annual Load Contributions and Losses by Source for Calibrated Metals2 Sub-Model

	Arsenic	
Loads/Losses	kg	% ²
Upstream	122	67
SS Tribs	18	10
LBD	29	16
Watts	4	2
CSOs	9	5
Total Input ¹	182	100
Export to Potomac	-4,630	-2,544

¹ Total Input is the sum of loads from upstream, SS Tribs, LBD, Watts and CSOs.

² % represents the percentage of total input (sum of all loads).

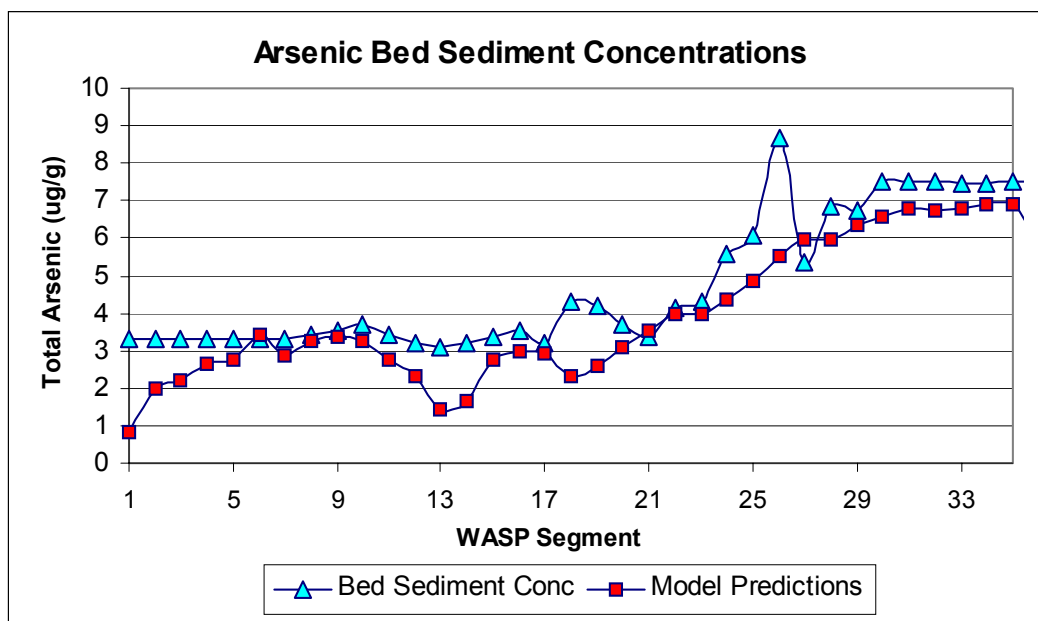


Figure 3-39. Arsenic Bed Sediment Results

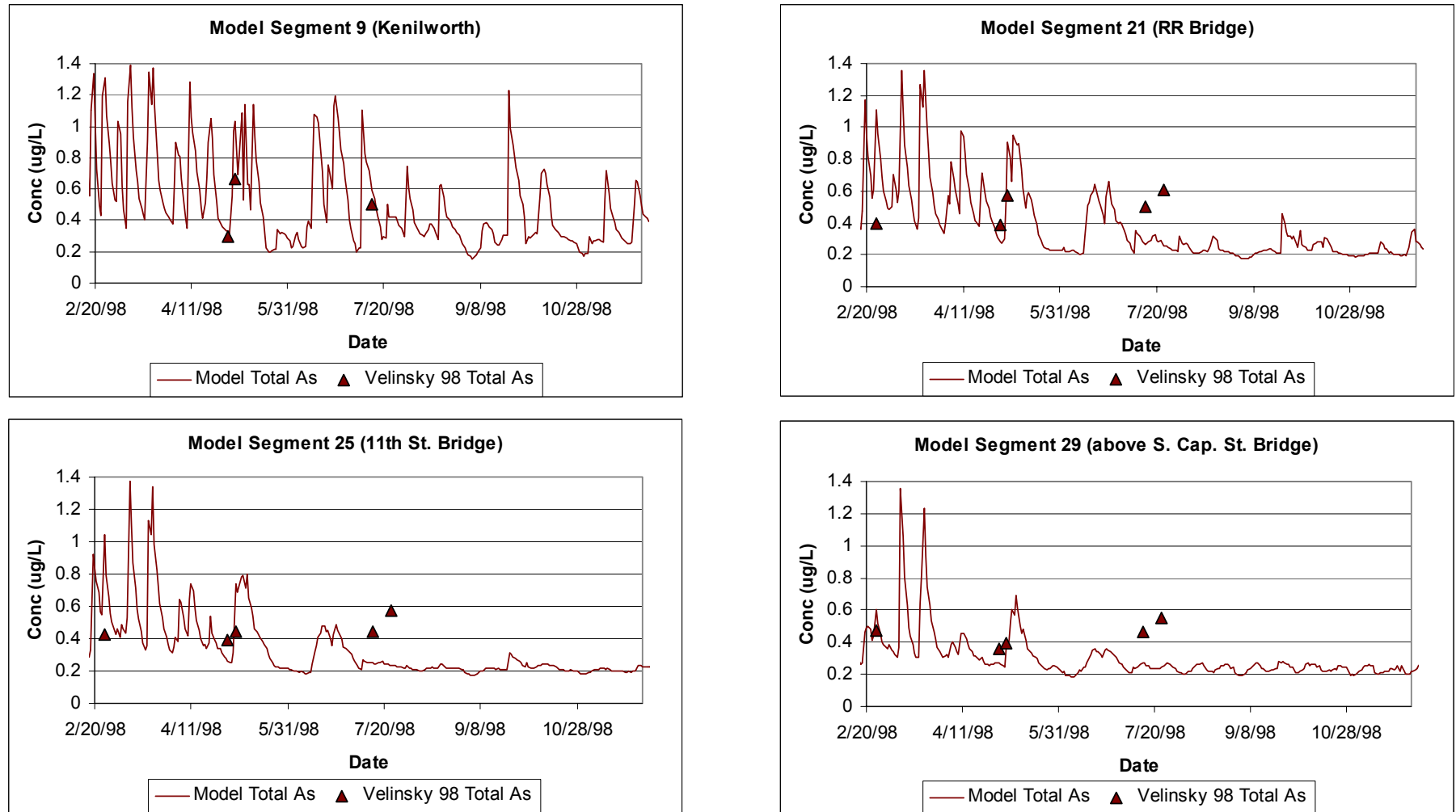


Figure 3-40. Predicted vs. Measured Water Column Concentrations for Total Arsenic (ug/L)

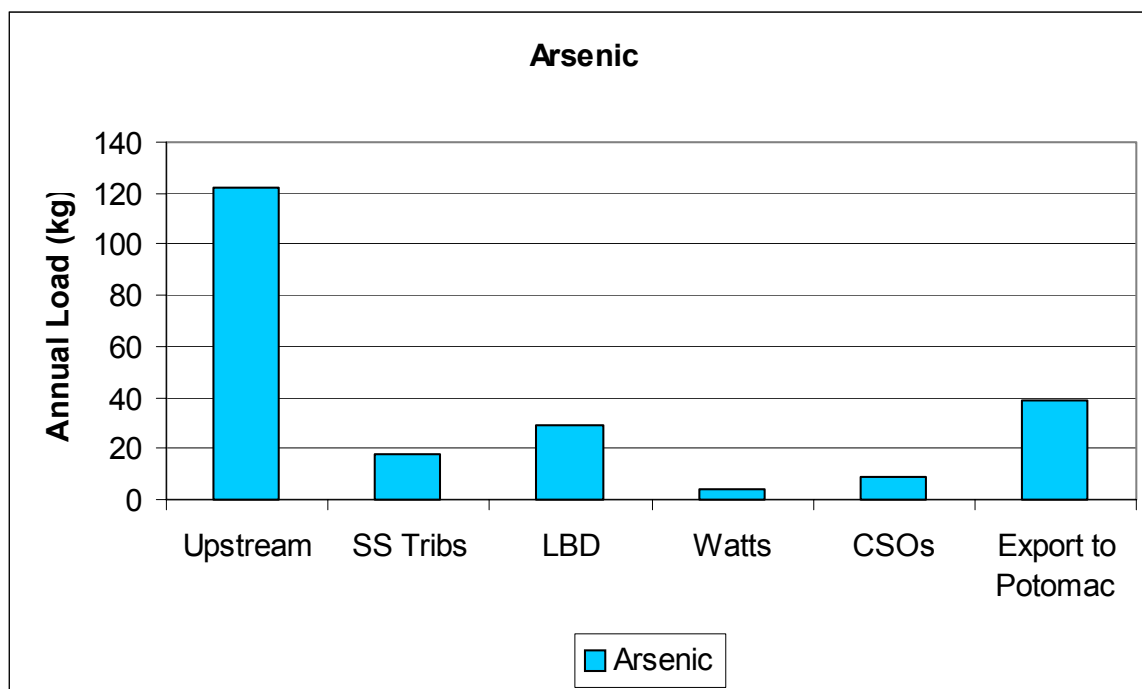


Figure 3-41. Summary of Average Annual Loads and Losses for Arsenic (Metals2) Sub-Model

3.3.3. PCBs Sub-Model

Fate Processes

Probable fate processes for PCBs include sorption, volatilization, biodegradation, and bioaccumulation (TOXNET, U.S. ACE 1997). It is uncertain whether photolysis is a significant degradation process as little experimental data exists to determine its importance (TOXNET). Oxidation and hydrolysis are not deemed to be important fate processes for PCBs in an aquatic environment (TOXNET, U.S. ACE 1997).

Volatilization from water surfaces can be expected, but adsorption to suspended solids and sediments limits the rate of volatilization, especially in the case of higher chlorinated congeners (TOXNET). A study conducted by Bamford et al. from March 1997 to March 1998 found that the tri- through pentachlorobiphenyls contributed approximately 90% of the annual PCB volatilization fluxes for both the Baltimore Harbor and the northern Chesapeake Bay.

In the atmosphere, PCBs primarily exist in the vapor phase but may become associated with particles as the degree of chlorination increases (TOXNET, U.S. EPA). Physical removal of PCBs from the atmosphere can occur through wet and dry deposition.

In sediments, mono-, bi-, and trichlorobiphenyls may degrade rapidly and tetrachlorobiphenyls slowly by aerobic microbial dechlorination, depending on the position of the chlorine atoms on the biphenyl ring (TOXNET, U.S. EPA, Cho et al.). Higher chlorinated biphenyls are resistant to aerobic biodegradation, but may be degraded anaerobically, by reductive dechlorination, to lower chlorinated PCBs (IPCS 1992). The extent of PCB dechlorination by biotic processes in sediments, however, depends on the PCB concentration and the population size of the dechlorinating organisms. It has been reported that microbial dechlorination does not take place at concentrations below 40 ppm (Cho et al., Rhee 1999, TOXNET).

Model Description

A TAM/WASP model has been set up for three groups of PCB homologs as shown in Table 1-2. The rationale for the groupings is based on similarities in molecular weights (MW), partition coefficients (K_d), Henry's Law coefficients (HLC), and biodegradation potential (Table 1-3).

Monochlorobiphenyls, which include congeners #1, #2, and #3, are currently not included in the model due to limited data support. Congener #1 has been found in significant quantities in the sediment (Velinsky and Ashley, 2001) but has not been reported in either the Anacostia River (Velinsky et al., 1999) or in the NE and NW Branches (Gruessner et al., 1998) water columns. Congener #2 has not been reported in any of the three studies. Congener #3 was detected by Velinsky and Ashley (2001) in the Anacostia River sediment, was reported as below the detection limit in the Gruessner et al. (1998) NE and NW Branches water column data set, and was not reported in the Anacostia River by Velinsky et al. (1999).

The decachlorobiphenyl (congener #209) is not included because it has neither been reported in the Gruessner et al. (1998) nor the Velinsky et al. (1999) water column data sets, and most of the

decachlorobiphenyl sediment data as reported by Velinsky and Ashley (2001) is below the detection limit. The limited amount of sediment data that does exist could be incorporated into the model; however, ICPRB found that it has little effect on model predictions.

Based on the likely fate processes described above, the only transport and fate processes simulated are advection and dispersion, absorption to the medium-grained and fine-grained sediment fractions, and volatilization.

Wet and dry deposition has not been included in the model because regional data for congeners or homologs is not available, and because ICPRB estimates, using non-site-specific data, indicate that wet and dry deposition contribute an insignificant amount to the total PCB load to the Anacostia River (see Table 3-9). Furthermore, Foster et al. (1999) state that “the relative abundance of hexa- and heptachlorobiphenyls in PCB transport ... indicated that the major source to the river was land based erosion rather than from direct atmospheric deposition ...”

Although bioaccumulation is considered a significant fate process, it has not been included in the model framework due to a lack of data and because WASP currently does not have the capability to simulate bioaccumulation. Biodegradation also has not been included in the model because, based on literature reviews, biodegradation in the sediment apparently does not take place below a concentration of 40 ppm, but nowhere in the river has a sediment concentration been reported above this threshold.

Input Parameters

Estimated baseflow and stormflow concentrations used for the load estimates can be found in Table 3-10. NE and NW Branches base and stormflow values are means, assuming log normal distributions, of data collected by Gruessner in 1995 and 1996 (Gruessner et al., 1998). Tidal sub-basin tributaries baseflow values are estimated to be the averaged NE and NW Branches baseflow concentrations. Tidal sub-basin tributaries stormflow, separate storm sewer (SS) system, and combined sewer overflows (CSO) estimates are based on data from the District’s MS4 monitoring activities (Nicoline Shelterbrandt, private communication), where non-detects (NDs) were estimated to be 0.00025 ug/L, which is about half the reported minimum detection limit (MDL) (Table 2-5). Upstream and downstream concentrations used in the load computations were increased based on sediment calibration results (Table 3-10) as discussed below.

Proposed input parameters for downstream boundary conditions, adsorption, and volatilization are listed in Table 3-11. Model boundary conditions at the confluence with the Potomac River are based on the average base and stormflow data of two stations reported in the Velinsky et al. (1999) water column data set. The proposed partition coefficients were calculated from site-specific NE and NW Branches baseflow data reported by Velinsky et al. (1998). The proposed molecular weights for the three PCB groups are weighted means based on the percent occurrence of congeners in the NE and NW Branches data set. The Henry’s Law coefficients represent the average value of all congeners in a given PCB group (Source: Brunner et al., 1990). Atmospheric concentrations are based on average Baltimore Harbor concentrations for each PCB group (Source: Bamford et al.). A comparison of estimated atmospheric concentrations with other regional air studies is presented in Table 3-12.

Model Results

The PCB model was run for two scenarios: a base scenario using calculated loads and a scenario in which loads were adjusted to calibrate to the sediment data (Table 3-10). A comparison of model predictions (last day of six year run) versus average bed sediment concentrations for each PCB group and scenario are presented in Figure 3-42. A mass balance for the loads by source, kinetic losses, and net export to the Potomac River is shown in Figure 3-43 for the loads adjusted scenario. The relative contribution of the sources and losses compared to total river load is provided in Table 3-13. Based on the mass balance analysis, it appears that the primary source of PCB1 in the Anacostia River is due to Lower Beaverdam, whereas the primary source for both PCB2 and PCB3 is due to upstream loading.

As can be seen in the figures, the base scenario underestimates sediment concentrations for all three PCB groups. When the upstream and downstream loads are increased by a factor of three, which is within our likely limit of uncertainty, the model performs reasonably well, although it fails to predict the spike in the sediment data observed in segment 28. In this segment, sediment concentrations are elevated due to the inclusion of historic 1995 Navy Yard data, which was derived by disaggregating Aroclor 1260 sediment concentration data into homologs based on Aroclor composition data by Frame (1996).

Model predictions of water column concentrations versus water column data collected by Velinsky et al. (1999) for each PCB group and scenario are shown in Figures 3-44 to 3-49. The base scenario tends to underestimate water column concentrations (Figures 3-44 to 3-46), but when the loads are adjusted as described above to calibrate the sediment layer, the model performs reasonable well (Figures 3-47 to 3-49). The base scenario underestimates both the sediment and water column concentrations, and therefore, it is possible that some sources of PCBs have not been captured by the current studies.

Sensitivity Runs

Two sets of runs were done to investigate the sensitivity of the baseline PCB model results on K_d values. In the first of set runs, K_d values for PCB1, PCB2, and PCB3 for both fine-grained and medium grained sediment fractions were all reduced by a factor of 1/4. In the second set of runs, all K_d values were increased by a factor of 10. Bed sediment results for these sensitivity tests are compared with baseline model runs in Figure 3-50. In these bed sediment results, the increased K_d 's tend to increase long-term bed sediment concentration predictions, and the decreased K_d 's tend to decrease long-term bed sediment concentration predictions, with the effects most pronounced for PCB1. Thus the 10-fold increase in K_d 's slightly improves the amount of total PCB mass predicted to accumulate in the bed sediment, and the factor of 1/4 decrease degrades the model's performance slightly in this respect. Water column results for the two sensitivity tests are shown in Figures 3-51 to 3-56. It can be seen in these figures that the factor of 1/4 decrease in K_d 's increases the model predictions of dissolved PCB concentrations in the water column, and the 10-fold increase in K_d 's decreases the dissolved water column concentrations.

Table 3-9. Annual Atmospheric Deposition of Total PCBs to the Anacostia River (kg/year)

TAM/WASP Toxic Screening Level Model for the Anacostia River - Preliminary Draft, 1/24/03

Chesapeake Bay - Regional¹		Chesapeake Bay - Urban¹		Baltimore²	
Wet Deposition	Dry Deposition	Wet Deposition	Dry Deposition	Wet Deposition	Dry Deposition
0.003	0.003	0.027	0.026	0.016 - 0.022	0.029 - 0.059

Calculations assume that the surface area of the Anacostia River is 3,300,300 m² and are based on data adapted from:

¹CBP (1999) and

²Joel Baker (private communication)

Table 3-10. Concentrations Used to Compute PCB Sub-Model Calibration Run Input Loads (ug/L)

Source	PCB1 Orig	Suggested PCB1 Multiplier	PCB1 Draft Final	PCB2 Orig	Suggested PCB2 Multiplier	PCB2 Draft Final	PCB3 Orig	Suggested PCB3 Multiplier	PCB3 Draft Final	Comment
NW Br Base	0.000597	x 3.0	0.00179	0.001897	x 3.0	0.005691	0.001058	x 3.0	0.003174	Concentration computed from 6 samples of Gruessner et al. (1998) 1995-96 data
NW Br Storm	0.000409	x 3.0	0.00123	0.006127	x 3.0	0.018381	0.004584	x 3.0		Concentration computed from 4 samples of Gruessner et al. (1998) 1995-96 composite data
NE Br Base	0.000577	x 3.0	0.00173	0.002630	x 3.0	0.007891	0.000823	x 3.0	0.002468	Concentration computed from 6 samples of Gruessner et al. (1998) 1995-96 data
NE Br Storm	0.000659	x 3.0	0.00198	0.008813	x 3.0	0.026439	0.007312	x 3.0	0.021937	Concentration computed from 4 samples of Gruessner et al. (1998) 1995-96 composite data
SS Trib Base	0.000585	x 3.0	0.00176	0.002337	x 3.0	0.007011	0.000917	x 3.0	0.002750	Estimated to be the averaged NE/NW Branches baseflow (Gruessner et al., 1998)
SS Trib Storm	0.007796	x 3.0	0.02339	0.014971	x 3.0	0.044913	0.004082	x 3.0	0.012245	Estimated to be the averaged DC MS4 monitoring data, with NDs at ½ DL.
CSO	0.007796	x 3.0	0.02339	0.014971	x 3.0	0.044913	0.004082	x 3.0	0.012245	Estimated to be the averaged DC MS4 monitoring data, with NDs at ½ DL.

Table 3-11. WASP Input Parameters for PCB Sub-Model

Process	Parameter	Units	PCB1	PCB2	PCB3	Source and Comment
Downstream Boundary Condition:						
	Potomac boundary concentration	ug/L	0.00031	0.00101	0.00080	Computed from Velinsky et al., (1999). Average base and stormflow concentrations of two sampling sites.
Adsorption:						
	K _d for fine-grained sediment	L _w /kg _s	50,000	172,000	554,000	Mean K _d based on site-specific baseflow data (Gruessner et al., 1998).
	K _d for medium-grained sediment	L _w /kg _s	13,000	43,000	139,000	Taken to be ¼ of the fine-grained sediment K _d . Based on best professional judgment
Volatilization:						
	Molecular Weight	g/mole	253	327	412	Weighted mean of congeners.
	Henry's Law Coefficient	atm – m ³ /mole	2.04E-04	8.81E-05	1.42E-05	Mean of congeners. Adapted from Brunner et al., 1990.
	Atmospheric Concentration	mg/L	4.22E-10	2.86E-10	0.0	Average Baltimore Harbor conc. for group. Adapted from Bamford et al.

Table 3-12. Range of Atmospheric Concentrations of PCB Homologs

PCB Homologs	Gaseous Phase Concentration Range in pg/m ³									
	Baltimore Harbor, MD ¹ Mar '97 - Mar '98	Baltimore, MD ² July '97	Chesapeake Bay, MD ² July '97	Northern Chesapeake Bay ³	Southern Chesapeake Bay ³	New Brunswick, NJ ³ Oct. '97 - May '99	Sandy Hook, NJ ³ Feb. '98 - Feb '99	Jersey City, NJ ³ July '98, Oct. '98 - May '99	Delaware River Estuary ⁴	Galveston Bay, TX ⁵ Feb. '95 - Aug '96
Mono									127 - 523 (est)	
Di	10 - 196								127 - 523 (est)	3.9 - 938
Tri	24 - 614	BDL - 188	BDL - 76	19.9 - 62.9	4.5 - 6.0	28.3 - 46.3	20.1 - 33.8	57.8 - 83.8	96 - 290	43.0 - 3428
Tetra	15 - 230	BDL - 279	1.3 - 122	15.8 - 19.3	5.2 - 7.7	9.1 - 30.9	9.6 - 30.6	21.8 - 56.0	65 - 288	44.3 - 1172
Penta	7.8 - 191	BDL - 68	3.8 - 55	6.8	4.8	16.1	13.5	26.5	45 - 195	5.1 - 210
Hexa	5.3 - 122	BDL - 50	6.6 - 38	4.4 - 10.1	5.9 - 10.2	5.4 - 6.0	5.0 - 5.2	9.9 - 10.4	9 - 37	4.4 - 159
Hepta		BDL - 8.5	0.9 - 6.8	1.8 - 2.3	1.7 - 2.7	0.9 - 2.0	0.7 - 2.1	1.7 - 2.6	4 - 9	ND - 305
Octa									0	ND - 4.7
Nona									0	ND - 3.2
Deca									0	ND - 13.3
Total PCB	64 - 1400	760 - 2220	290 - 990	510	210	526 ± 395	439 ± 303	960 ± 802	472 - 1865	207.8 - 4783.1

BDL - below detection limit

ND - not detected

¹ Bamford et al.

² Adapted from Brunciak et al., 2001

³ Adapted from Brunciak et al., 2000

⁴ Liao, 2001

⁵ Park, 2000

Table 3-13. Average Annual Load Contributions and Losses by Source for Calibrated PCB Sub-Model

Loads / Losses	PCB1		PCB2		PCB3	
	kg	%²	kg	%	kg	%
Upstream	0.117	19.7	1.126	54.2	0.824	75.5
SS Tribs	0.143	24.1	0.293	14.1	0.084	7.7
LBD	0.242	40.8	0.471	22.7	0.130	11.9
Watts	0.035	5.9	0.071	3.4	0.020	1.9
CSOs	0.057	9.5	0.117	5.6	0.034	3.1
Total Input ¹	0.594	100	2.078	100	1.092	100
Kinetic Losses	-0.080	-13.5	-0.082	-3.9	-0.005	-0.5
Export to Potomac	-0.242	-40.7	-0.702	-33.8	-0.330	-30.2

¹ Total Input is the sum of loads from upstream, SS Tribs, LBD, Watts and CSOs.

² % represents the percentage of total input (sum of all loads).

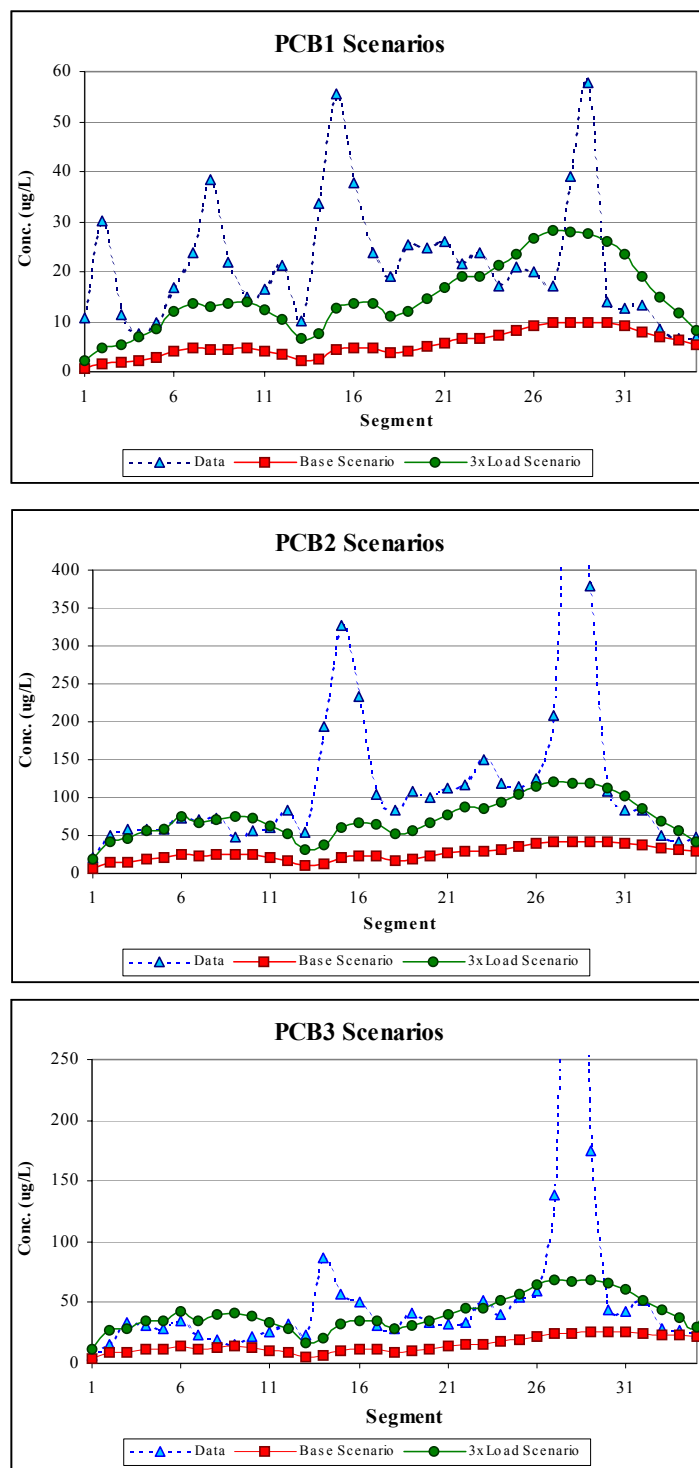


Figure 3-42. PCB3 Bed Sediment Results - Base Scenario and All Loads x 3

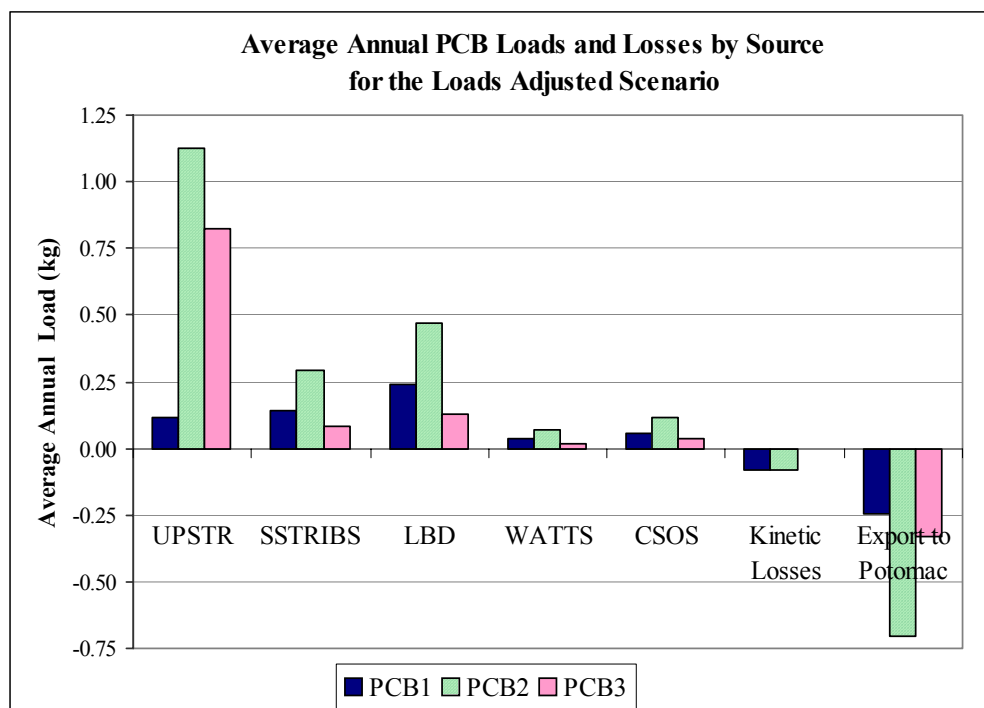


Figure 3-43. Summary of Average Annual Loads and Losses for the Calibrated PCB Sub-Model

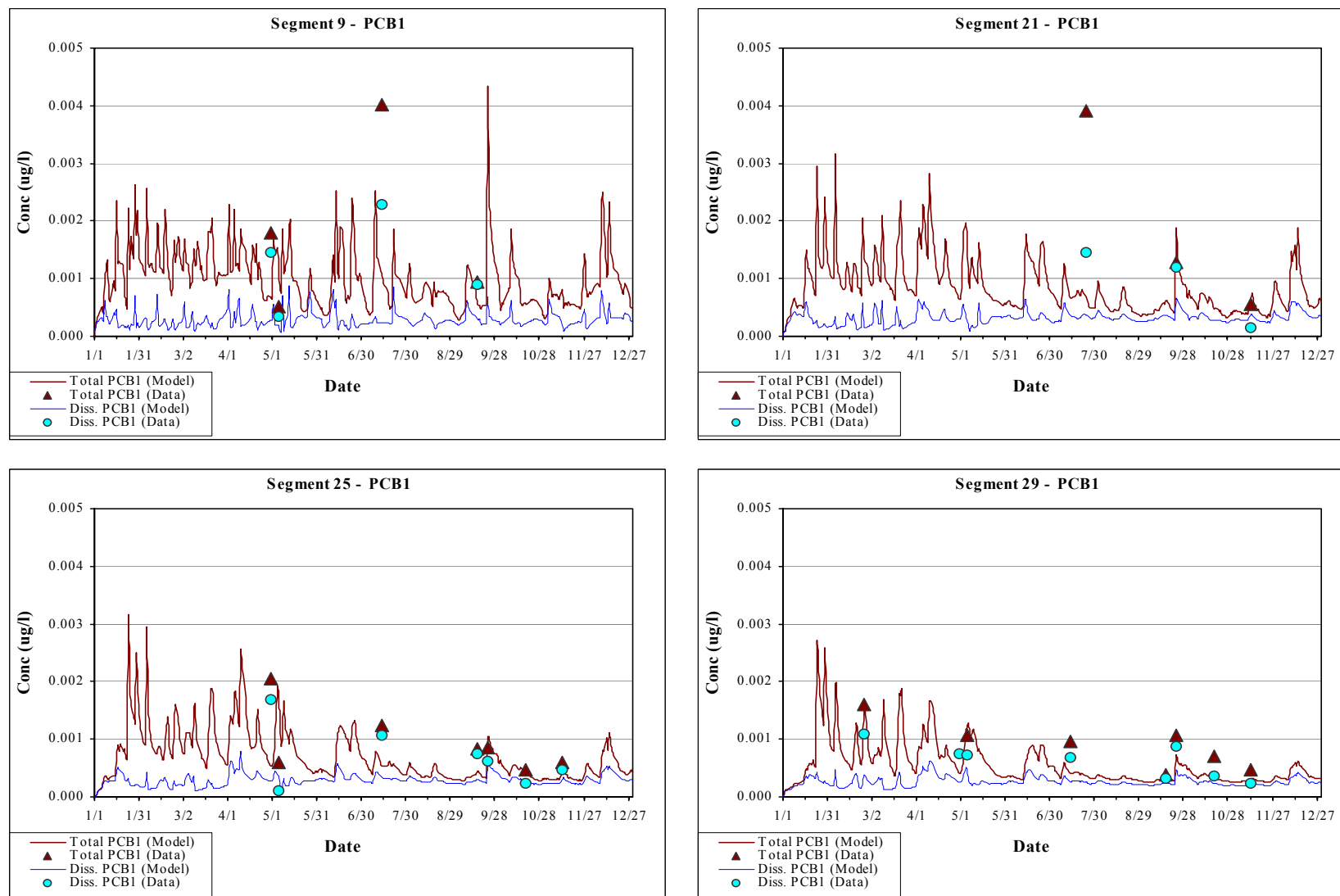


Figure 3-44. PCB1 Water Column Results for the Base Scenario

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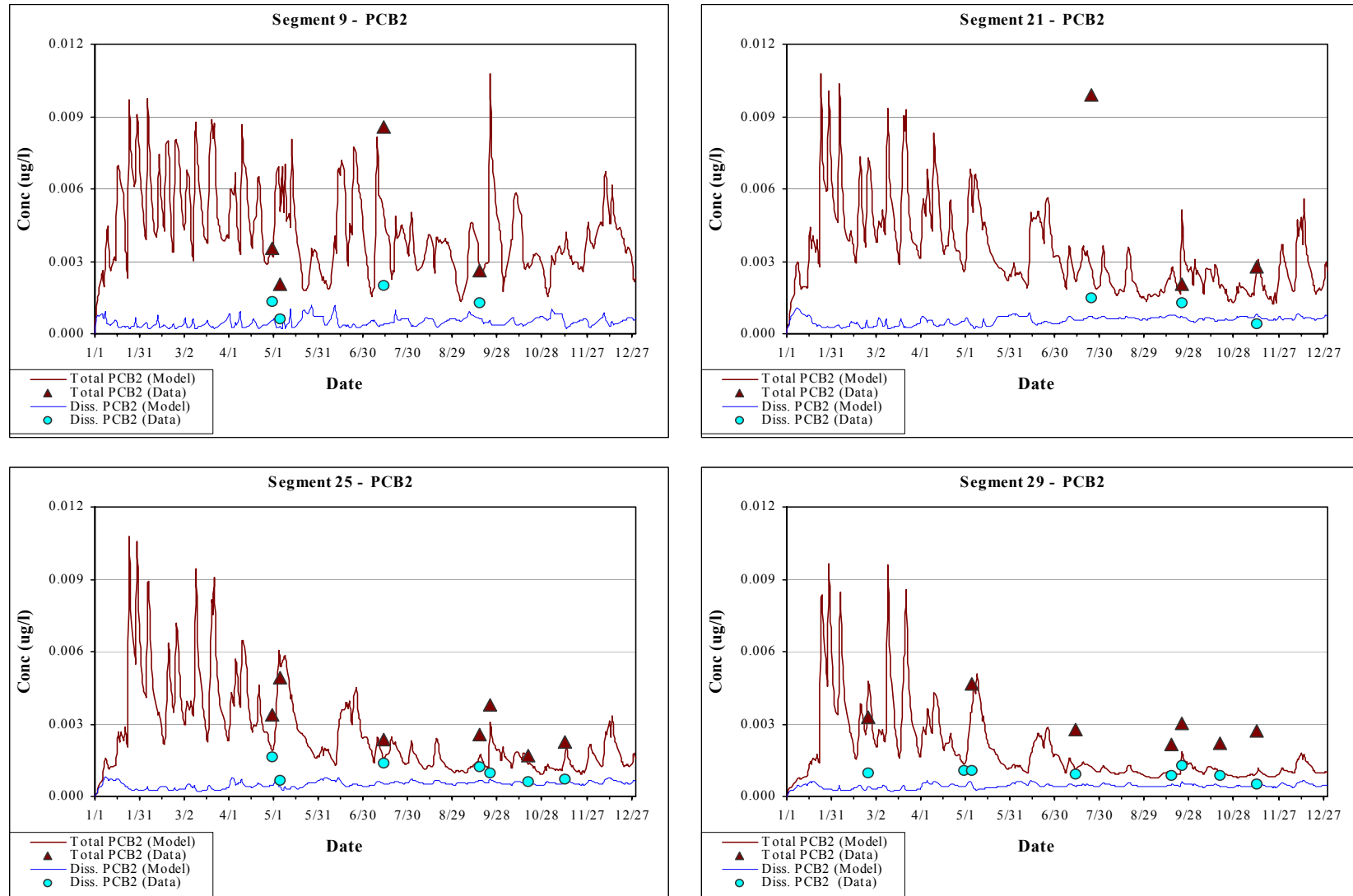


Figure 3-45. PCB2 Water Column Results for the Base Scenario

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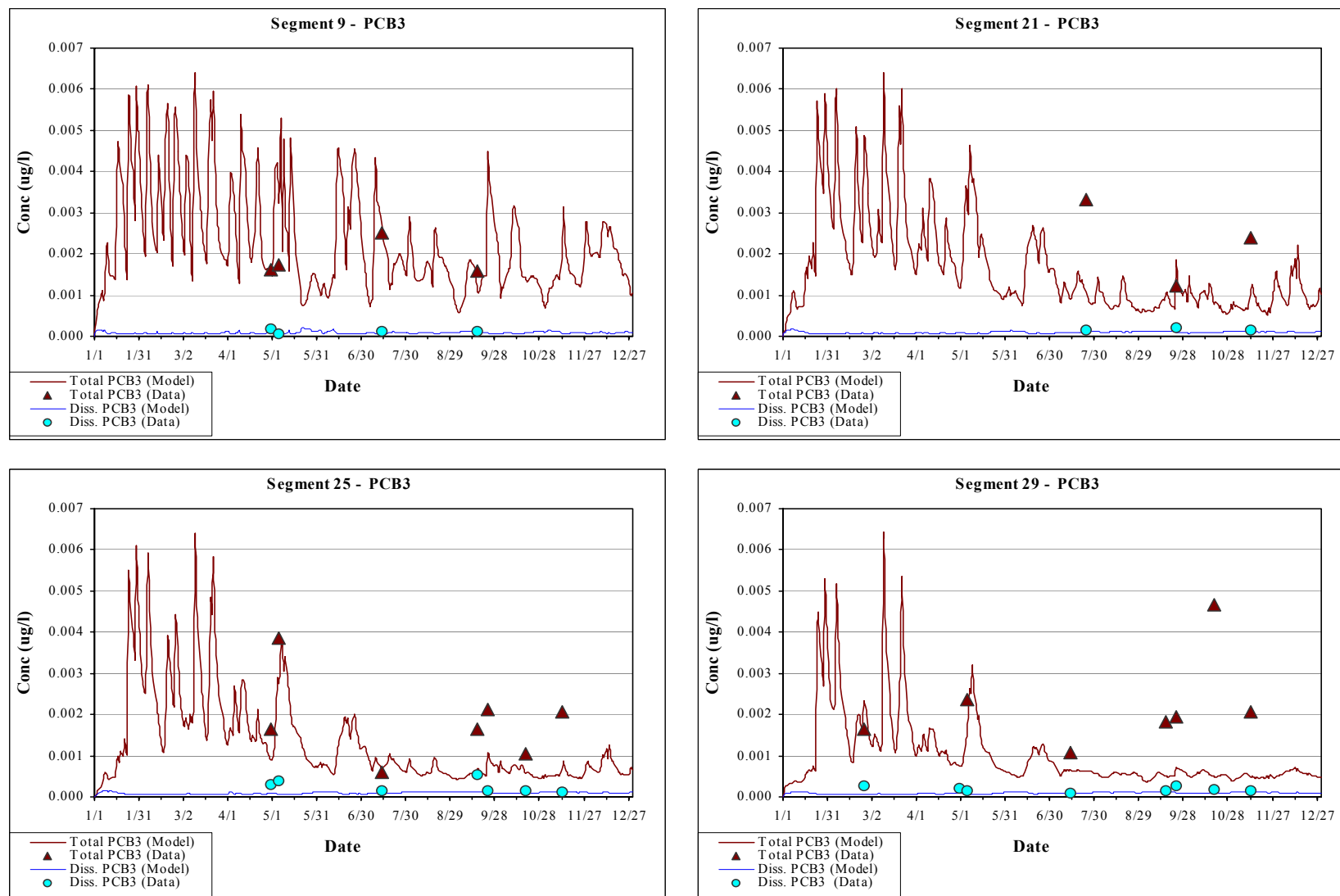


Figure 3-46. PCB3 Water Column Results for the Base Scenario

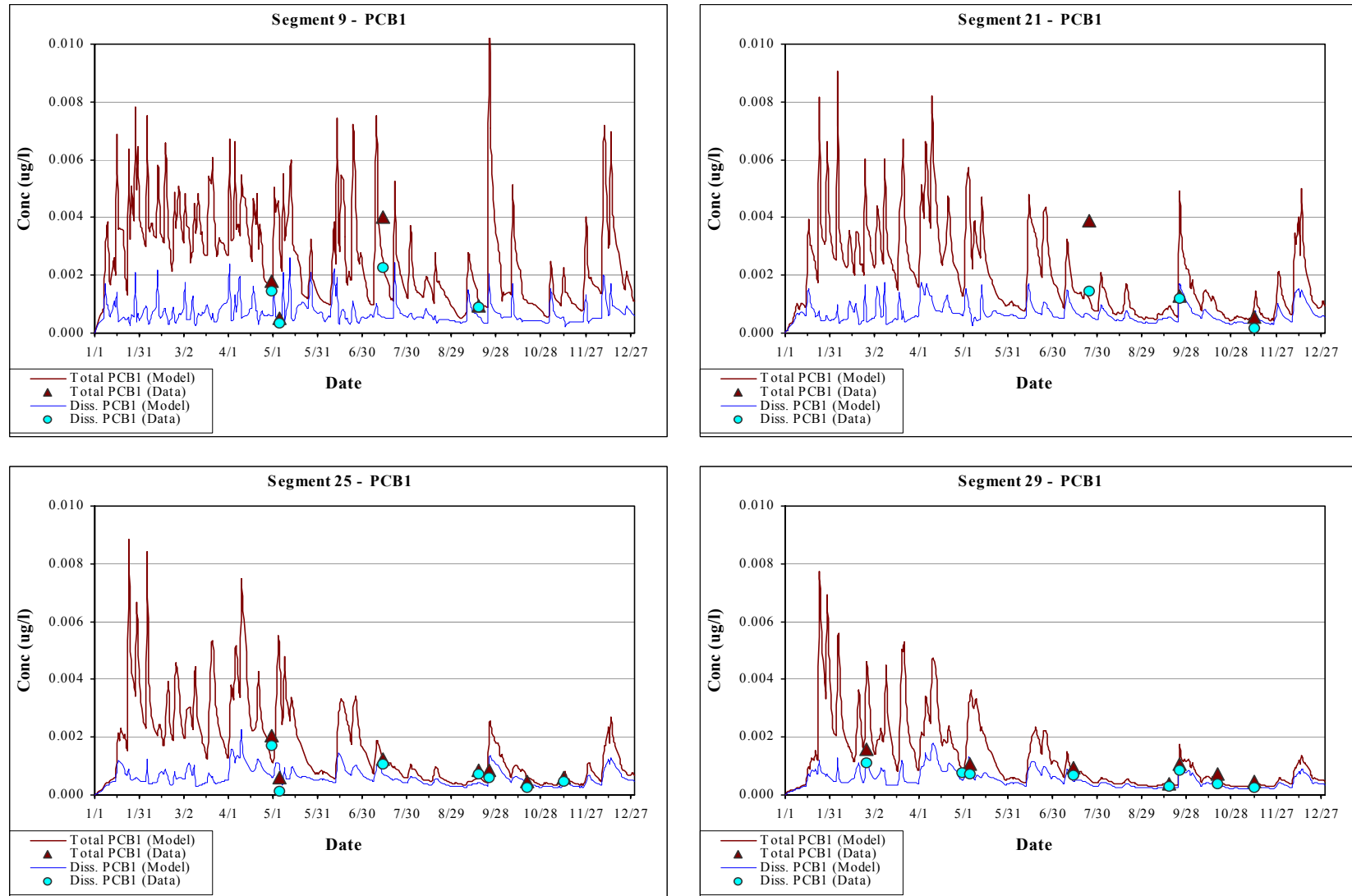


Figure 3-47. PCB1 Water Column Results for the Calibrated (3 x Loads) Scenario

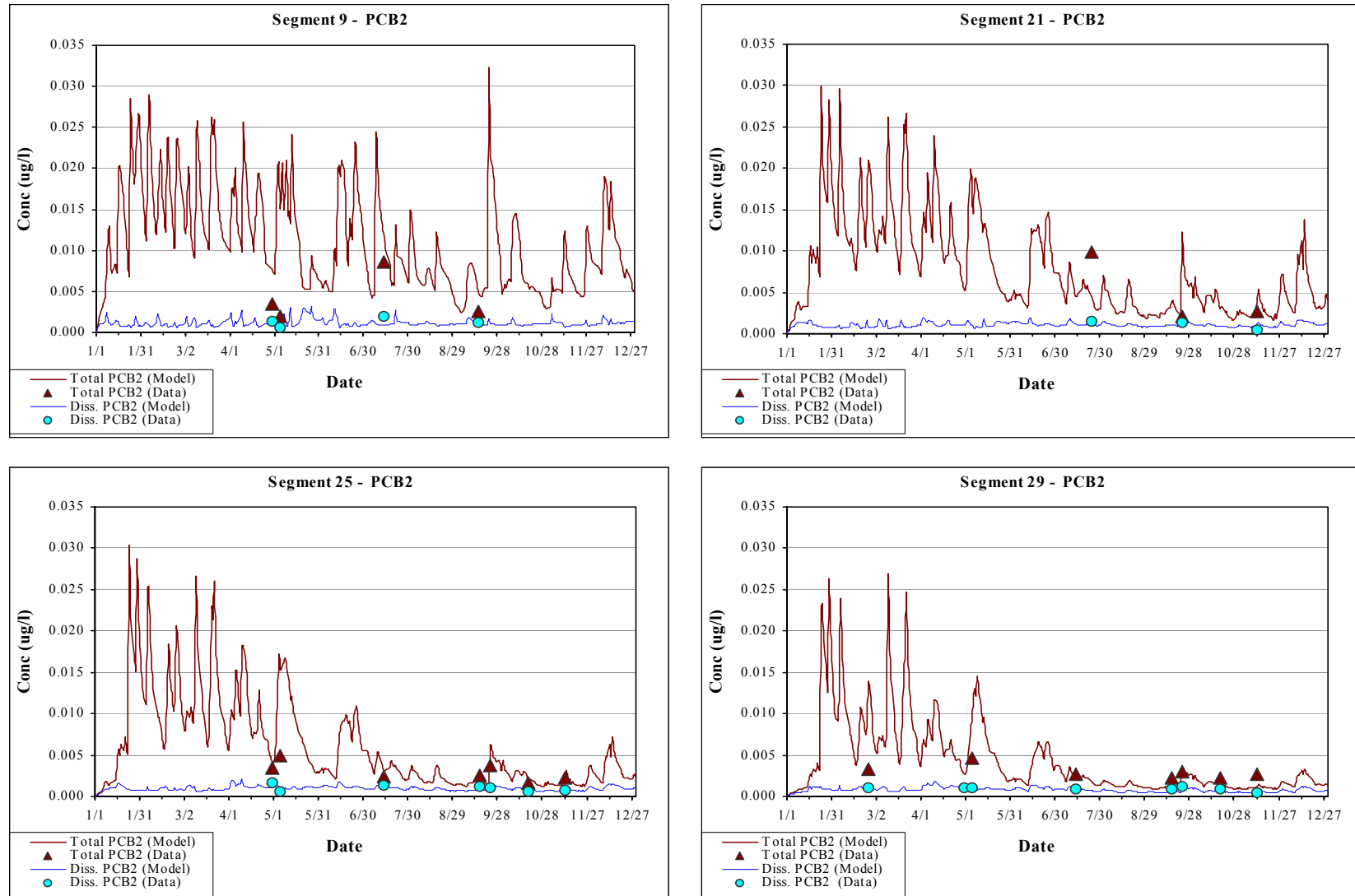


Figure 3-48. PCB2 Water Column Results for the Calibrated (3 x Loads) Scenario

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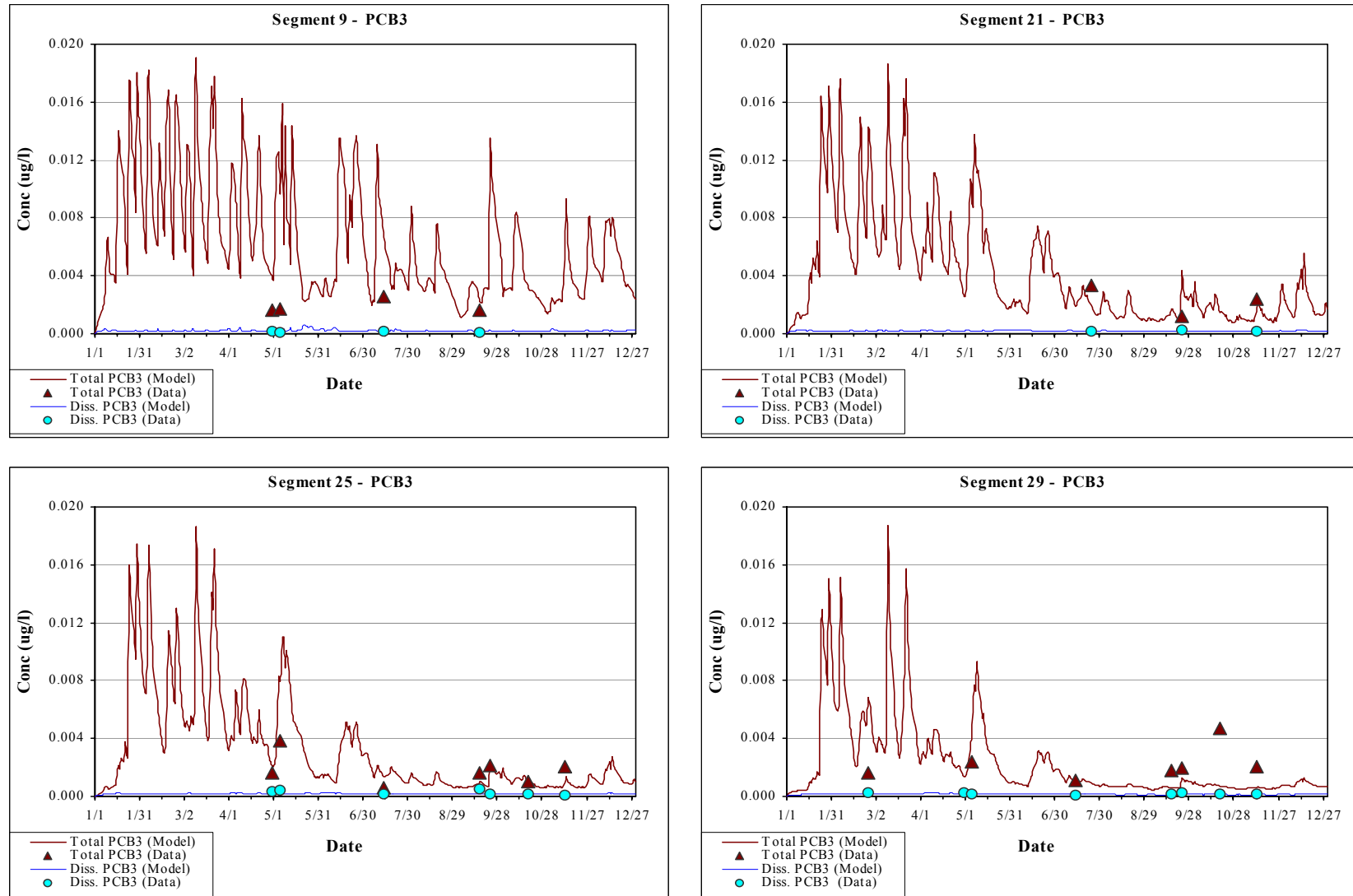


Figure 3-49. PCB3 Water Column Results for the Calibrated (3 x Loads) Scenario

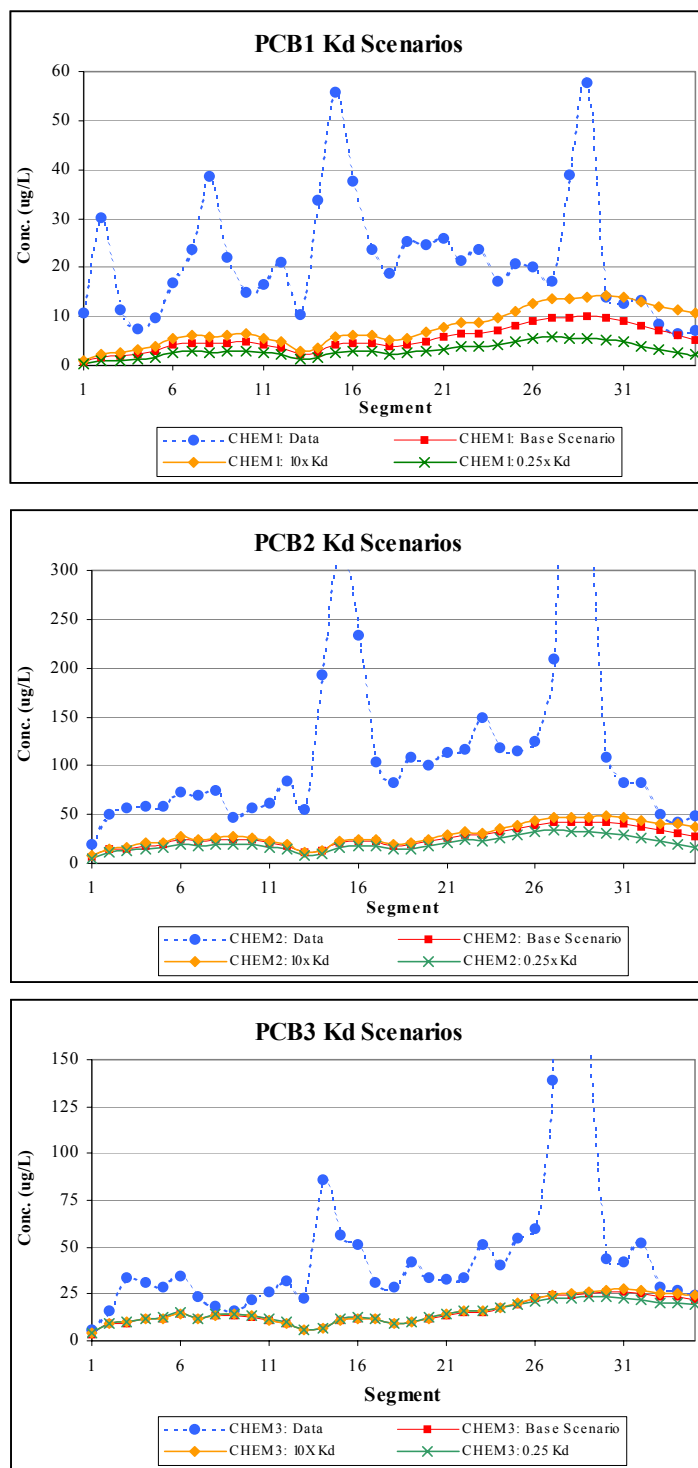


Figure 3-50. PCB Bed Sediment Results - Both K_d 's x 10; x 1/4

TAM/WASP Toxic Screening Level Model for the Anacostia River - Preliminary Draft, 1/24/03

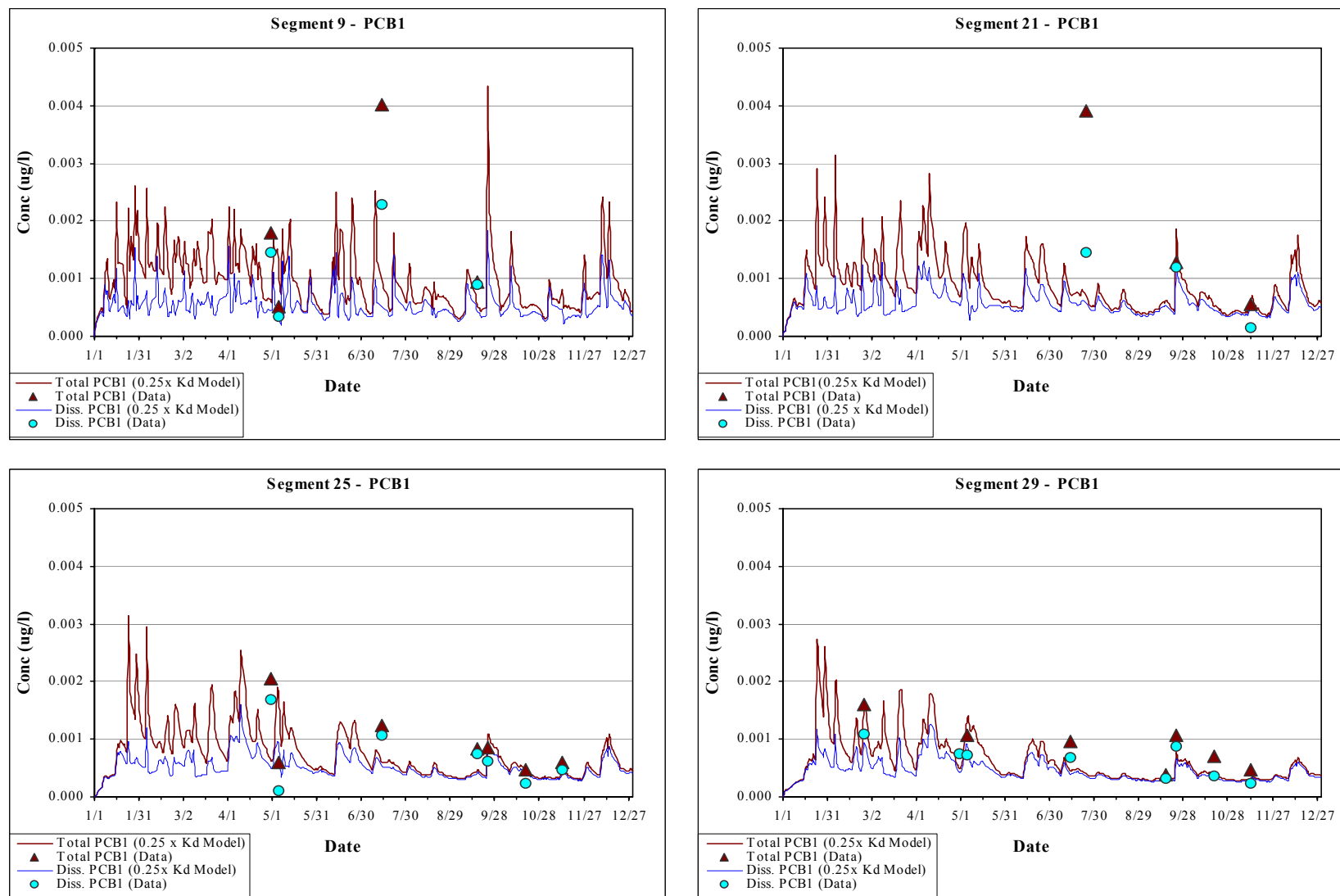


Figure 3-51. PCB1 Water Column Results - Both K_d 's x 1/4

TAM/WASP Toxic Screening Level Model for the Anacostia River - Preliminary Draft, 1/24/03

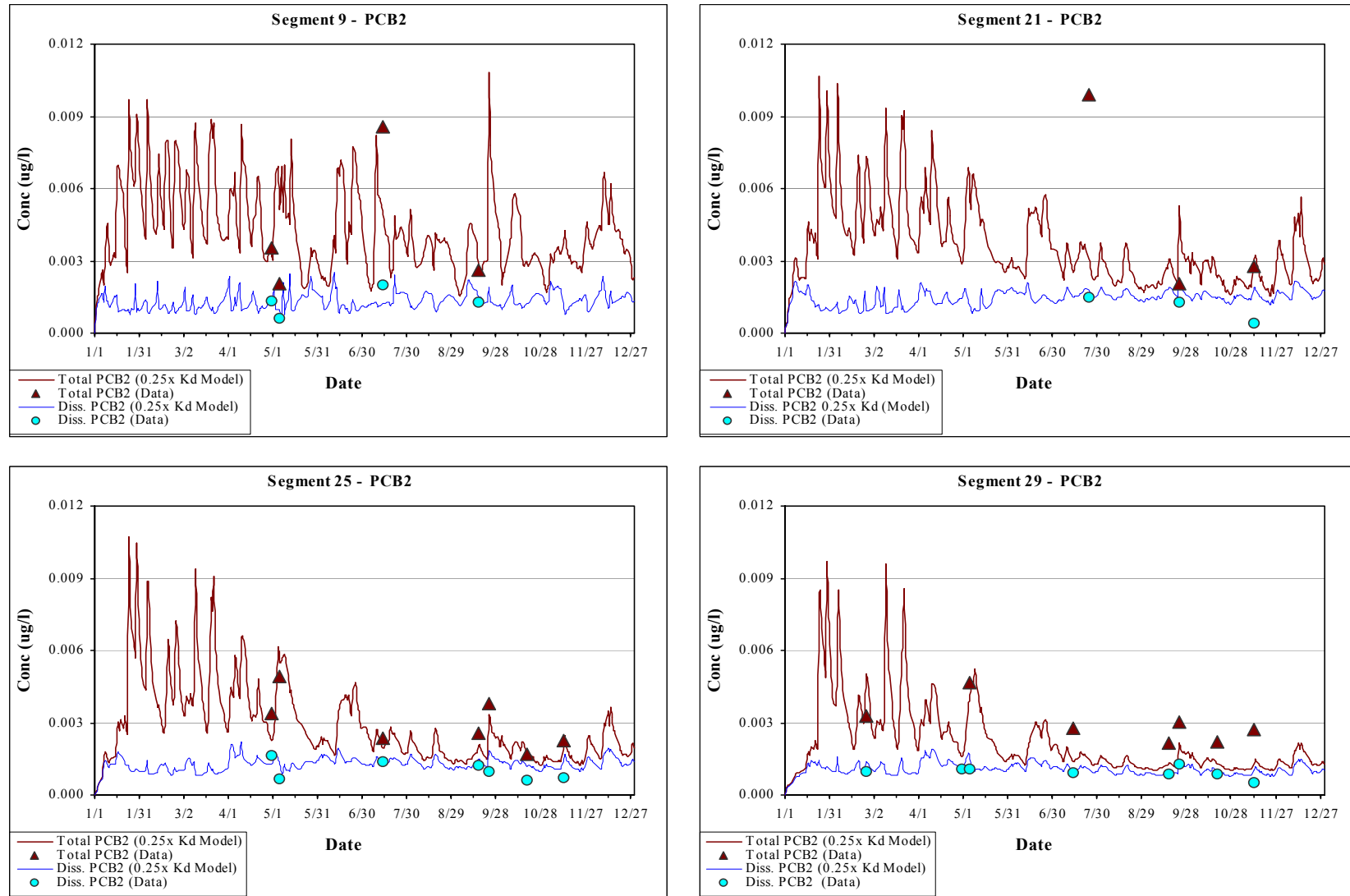


Figure 3-52. PCB2 Water Column Results - Both K_d 's x 1/4

TAM/WASP Toxic Screening Level Model for the Anacostia River - Preliminary Draft, 1/24/03

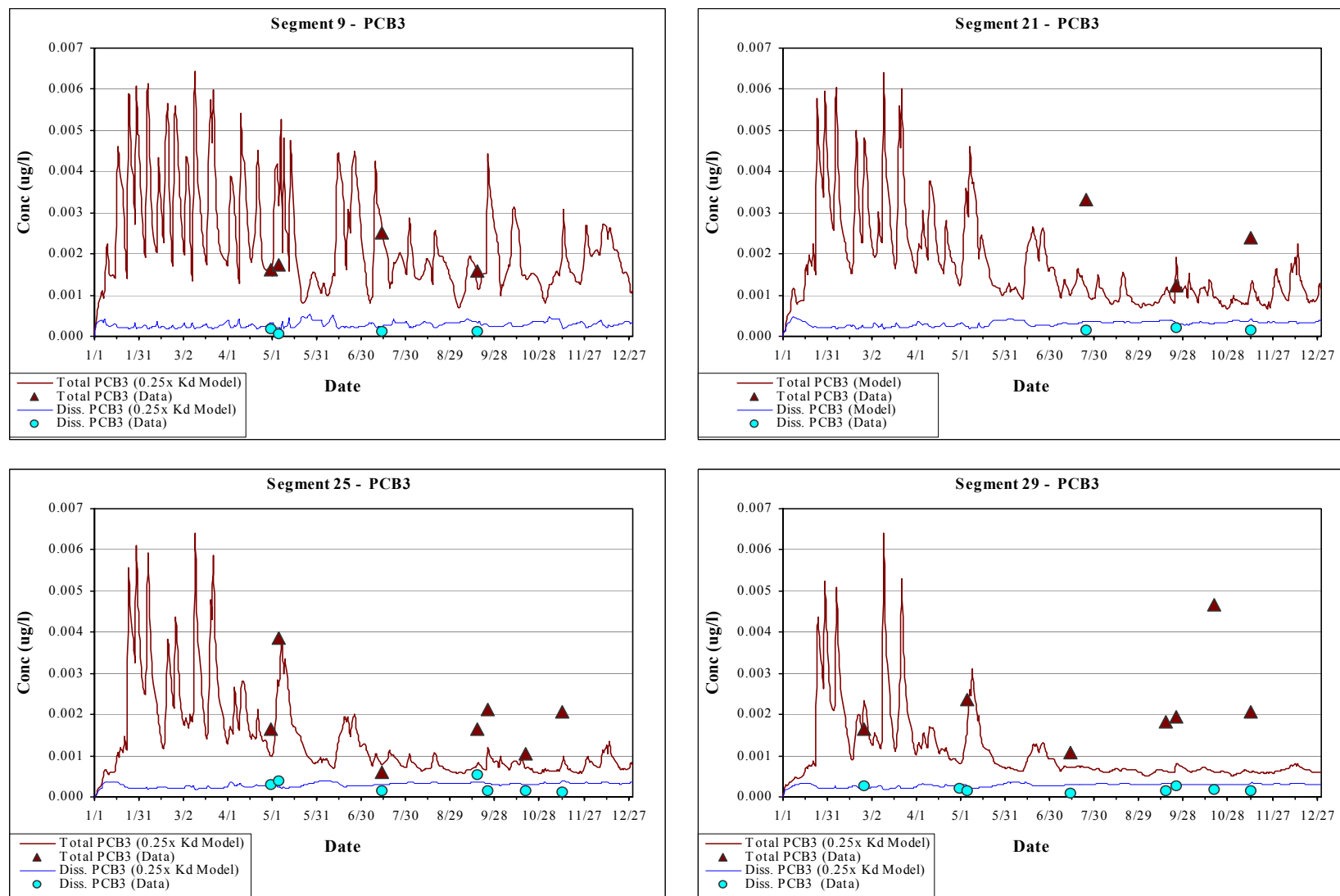


Figure 3-53. PCB3 Water Column Results - Both K_d 's x 1/4

TAM/WASP Toxic Screening Level Model for the Anacostia River - Preliminary Draft, 1/24/03

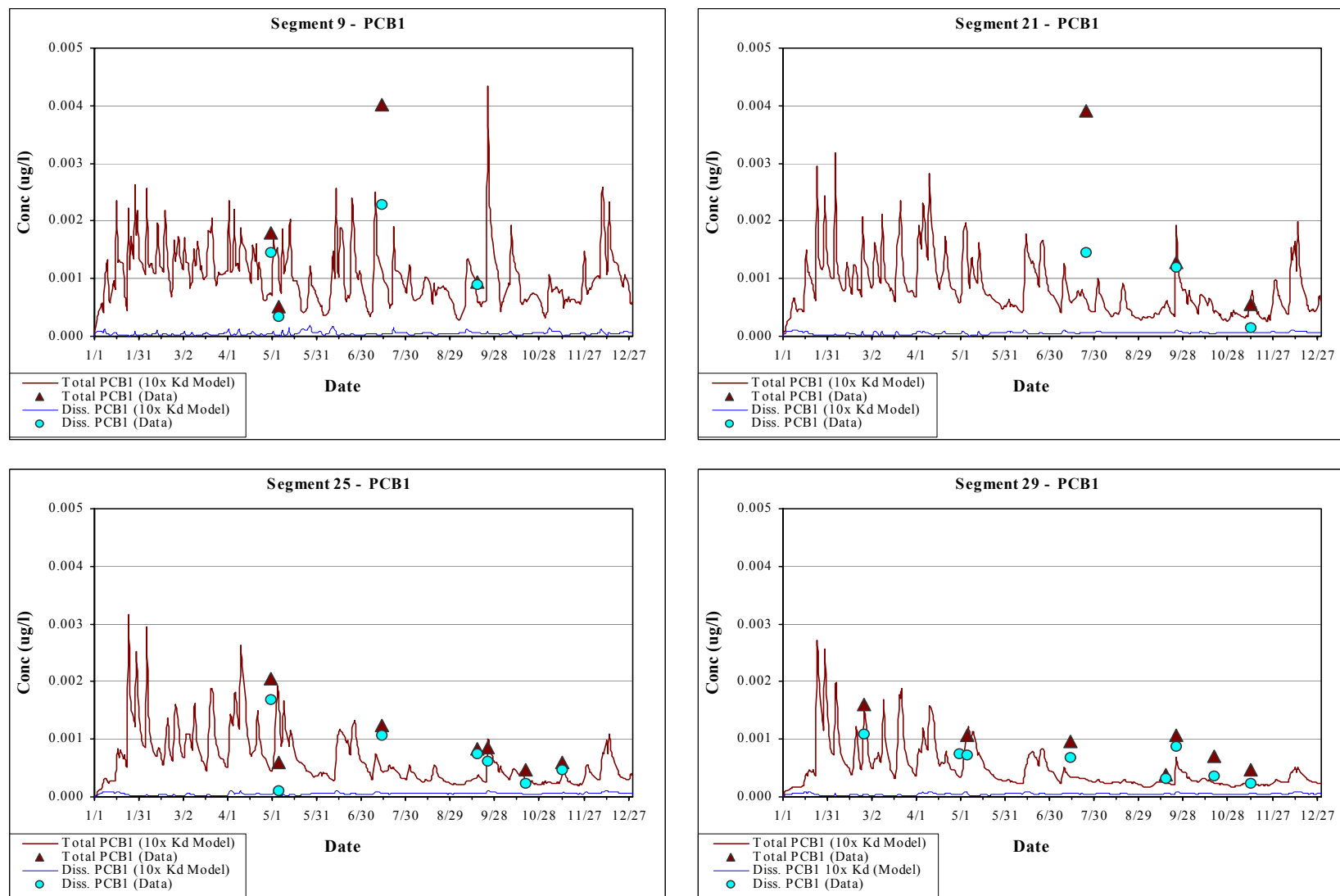


Figure 3-54. PCB1 Water Column Results - Both K_d 's x 10

TAM/WASP Toxic Screening Level Model for the Anacostia River - Preliminary Draft, 1/24/03

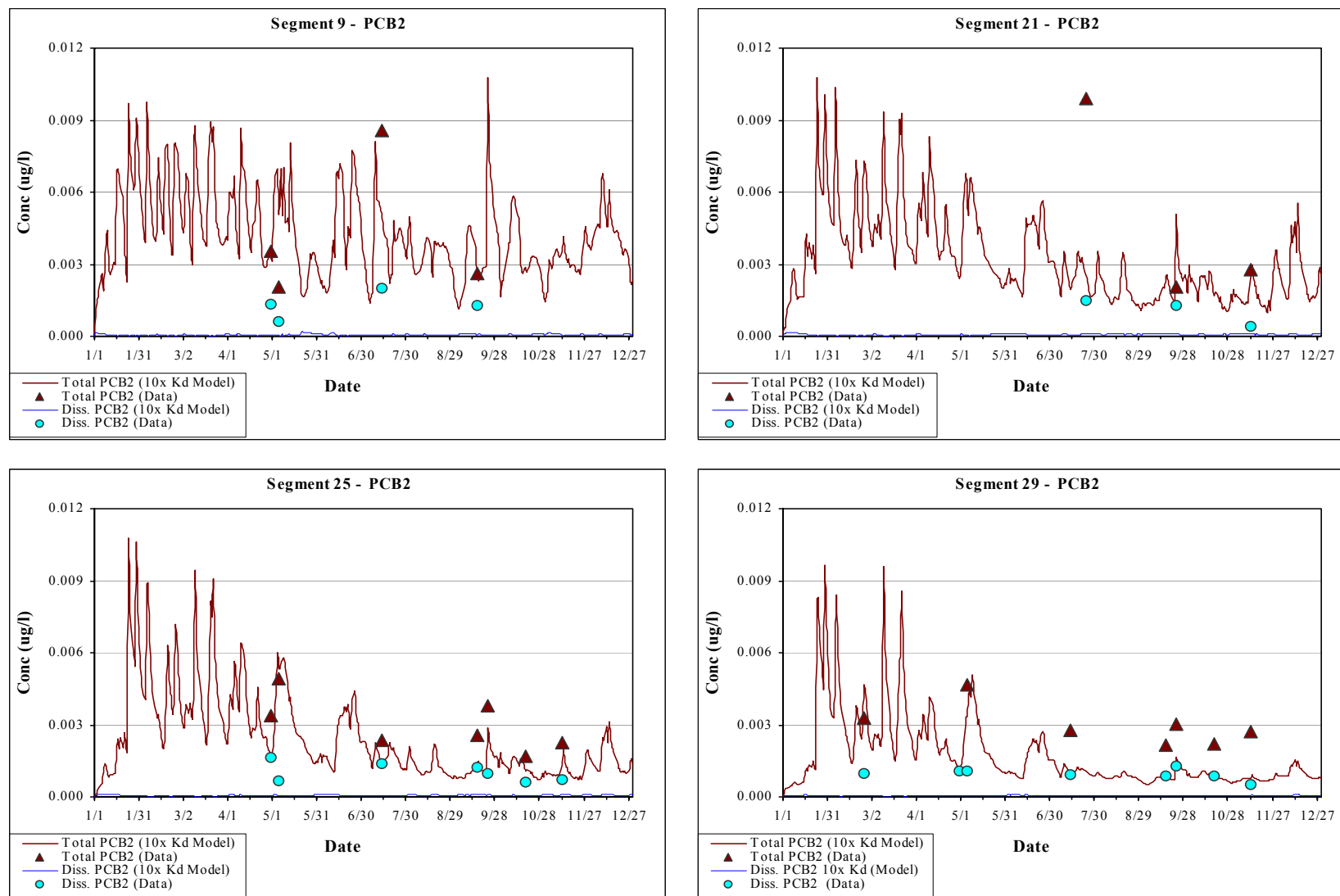


Figure 3-55. PCB2 Water Column Results - Both K_d 's x 10

TAM/WASP Toxic Screening Level Model for the Anacostia River - Preliminary Draft, 1/24/03

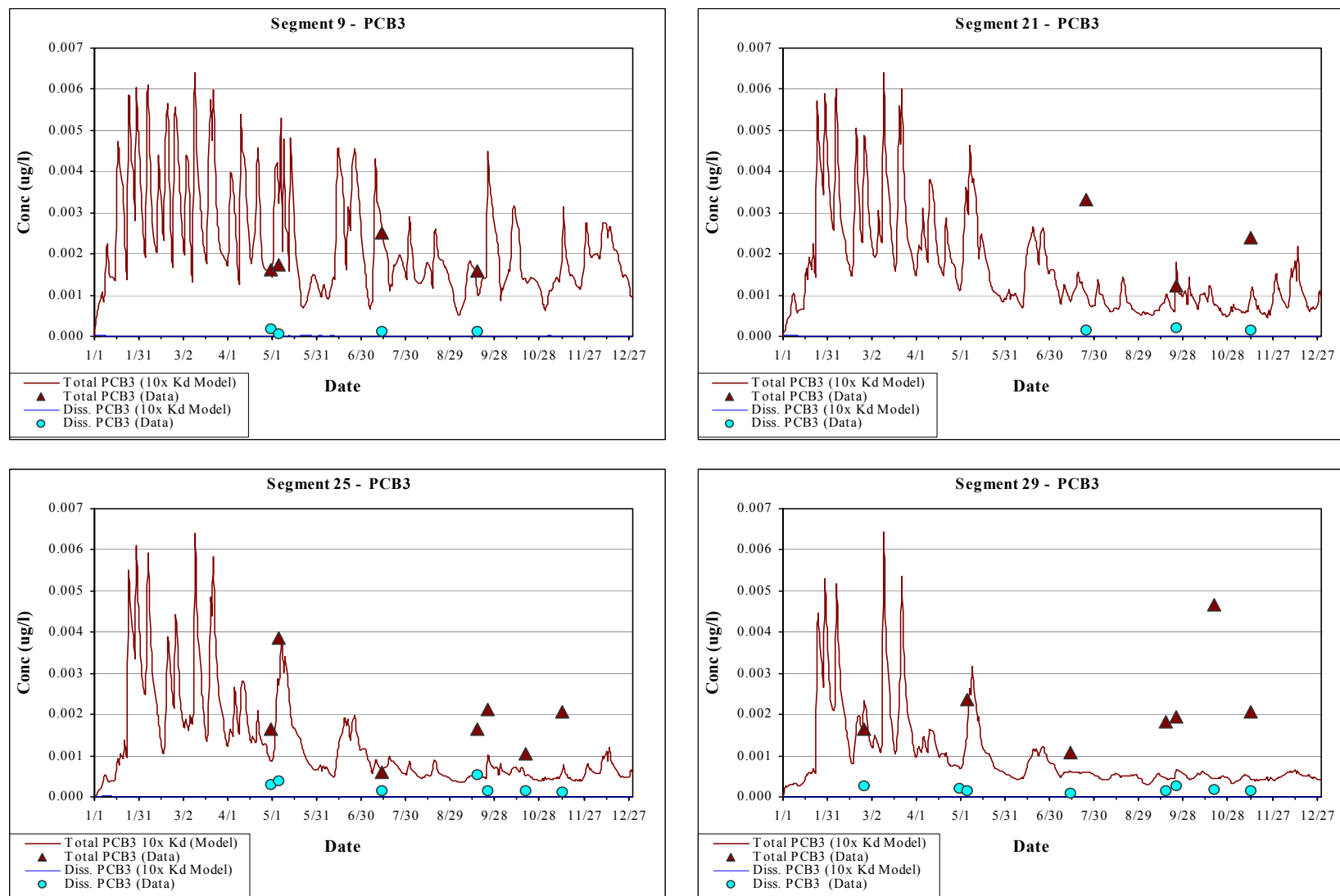


Figure 3-56. PCB3 Water Column Results - Both K_d 's x 10

3.3.4. PAHs Sub-Model

Model Description

The TAM/WASP PAH sub-model has been set up to simulate the fate and transport of 3 groups of PAHs representing a total of 16 chemicals, distributed by number of benzenoid rings and molecular weight, as discussed in Chapter 1 (see Tables 1-2 and 1-4). The sixteen PAHs considered in the model were chosen for reasons of data consistency, because all 16 were included in both the study of Northeast/Northwest Branch loads by Gruessner et al. (1998) and the study on bed sediment concentrations by Velinsky and Ashley (2001). The transport and fate processes simulated include advection and dispersion, absorption to the medium- and fine-grained sediment fractions, first-order degradation, and volatilization.

Input Parameters

Estimated baseflow and stormflow concentrations are given in Table 3-14. NE and NW Branch values represent means (assuming log normal distributions) of data collected by Gruessner in 1995 and 1996 (Gruessner et al., 1998). Tidal sub-basin, separate storm sewer (SS) system, and combined sewer overflows (CSO) values are estimates because detection limits for available stormwater monitoring data from the District's MS4 monitoring program (Nicoline Shelterbrandt, private communication) were not sufficiently low enough to be applicable. For example, the average PAH detection limit for the MS4 was 800 ng/L, whereas the average PAH detection limit in the Gruessner et al. (1998) study was 0.02 ng/L. Therefore, the values are derived by averaging upstream concentrations. Tidal sub-basin tributary baseflow and groundwater concentrations are estimated based on the NE/NW Branches baseflow analysis.

Proposed input parameters for downstream boundary conditions, adsorption, degradation, and volatilization are provided in Table 3-15. In addition, a boundary condition was specified for pore-water dispersion of PAHs at segment 24 to incorporate the impact of Washington Gas on the Anacostia River. Boundary condition PAH estimates at this segment were based on average sediment concentrations of seven samples collected along the shoreline adjacent to the Washington Gas former manufactured gas plant site during a 1995 Washington Gas study. This data was obtained from the AWT/NOAA database. The alternative and more traditional approach was to incorporate the flux of PAHs from Washington Gas into the model as a load. Groundwater concentrations of some PAHs at Washington Gas have been estimated (Hydro-Terra, Inc., 1998). However, there are a significant amount of non-detects in the data due to a high detection limit (10 ug/L) and several analytes in PAH group 3 were not included in the data set. Estimated yearly loads based on both approaches are presented in Table 3-16. ICPRB feels the pore water diffusion approach is more appropriate because data support is more complete and estimated loads are reasonable when compared with the groundwater estimates (Table 3-16).

Proposed distribution coefficients for the 3 PAH groups are shown in Table 3-15. These values were estimated from site-specific NE/NW branches baseflow data.

First-order lumped degradation rate constants were incorporated into the PAH model to represent the combined impacts of biodegradation and photolysis and were estimated based on reported literature

values, as shown in Table 3-15 (Aronson et al., 1999 and Mackay et al., 1992). Degradation of PAHs was modeled as a first-order rate constant in the model primarily due to a lack of PAH water column data for calibration and the need for biodegradation and photolysis rate estimates for the Anacostia River. Literature review indicated a trend towards an increase in degradation with decreasing molecular weight and increased degradation in water than in sediment. Individual PAH biodegradation rates reported in literature cover a wide range (Aronson et al., 1999 and Mackay et al., 1992). For example, the minimum reported rate constant for biodegradation of benzo[a]pyrene was 6×10^{-5} (per day) and the maximum was reported as 0.057 per day (Aronson et al., 1999).

Volatilization parameters are shown in Table 3-15. Atmospheric PAH concentrations were not available for the Anacostia watershed. Therefore, atmospheric concentrations were estimated based on available regional data for urban watersheds as shown in Table 3-17 (Bamford et al., 1999, Gustafson and Dickhut, 1997).

Wet and dry deposition has not been included in the model because data is not available for the Anacostia River. However, PAH wet and dry deposition estimates were obtained for the Chesapeake Bay watershed (CBP) and for Baltimore, Maryland, a comparable urban area (Offenberg and Baker, 1999). This data was compared with estimated loadings from the NE/NW branches and determined to be negligible for the Anacostia River, as shown in Table 3-18.

Model Results

The PAH model was run for 3 scenarios: with and without the Washington Gas exchange component with calculated upstream and downstream loads and with the Washington Gas component with loads adjusted to calibrate to the sediment data.

All 3 scenarios included the kinetic processes described above. A comparison of model predictions (last day of 6-year run) versus bed sediment concentration data is presented for each chemical grouping in Figure 3-57. There were two water column data sets available to compare model predictions of water column concentrations based on the calibration scenario for PAHs. Katz et al. (2000) provided PAH water column estimates resulting from one sampling event (July 12, 2002) at several locations along the Anacostia. Results from this comparison are provided in Figure 3-58. In addition, there was data available for sorbed PAHs in the water column from Coffin et al. (1998) for several events during the November 1997 - May 1998 time frame. Results from this analysis are provided in Figures 3-59 - 3-61. A mass balance for the calibrated model is presented in Figure 3-62 to illustrate loads by source, the impact of Washington Gas dispersion, total kinetic losses, and net export to the Potomac River. The relative contribution of each source and loss compared to total load is provided in Table 3-19.

Model results for the first scenario in which Washington Gas was not included as a dispersive boundary exchange (Figure 3-57, *basenoWG*) indicate that PAH loading from the NE/NW branches is not the sole source of PAHs in the sediments of the tidal Anacostia River. Inclusion of the Washington Gas component in the second scenario (Figure 3-57, *baseWG*) did capture some of the peak in PAH concentrations at segment 24, but overall, concentrations were still underestimated. In the third scenario, upstream and downstream loadings of PAHs were doubled in an effort to calibrate the model

(Figure 3-57, *2xloads WG*). Model results in this scenario account reasonably well for mass inputs of PAH into the tidal portion of the Anacostia River. However, it is obvious that there are some sources of PAHs in the tidal portion of the Anacostia that have not been captured based on available data.

Comparison of model predictions of water column concentrations with the Katz et al. (2000) event data indicate that the model is overestimating PAH concentrations in the water column for this particular day, especially for PAH groups 2 and 3 (Figure 3-58). Comparison of model predictions of sorbed PAHs with Coffin et al. data generally indicates an overestimation of PAH water column concentrations. However, this could be explained by uncertainties associated with the data. For example, there were two chemicals not included in the Coffin et al. analysis, 2-methyl naphthalene in PAH group 2 and perylene in PAH group 3. Also, exact sampling dates are not clear. Finally, there were several gaps in the Coffin et al. data set for PAH groups 1 and 3 in which data was provided for a particular chemical during some sampling events but not for all events. It was assumed that these chemicals were not detected (although no detection limits were provided). However, it is also possible that all samples were not measured for these chemicals.

Based on the results of this analysis, it appears that the primary source of PAHs in the Anacostia River is due to upstream loading, contributing over 50% of the total load as shown in Table 3-19. Kinetic losses Table 3-20.

Additional water column data is necessary to further calibrate the model, as it appears that there are some sources downstream that have not been captured in the data currently available. Nevertheless, ICPRB feels that the PAH model, as currently configured, is adequate to assist the District in its TMDL allocations for the tidal Anacostia River.

Model Sensitivity Analysis

The interactions of PAHs were investigated to test the model sensitivity to degradation. There is little available information to reliably estimate the pathways or rates of degradation of individual PAHs into other PAHs. As a sensitivity test, the model was run to simulate the degradation of higher-molecular weight PAHs into lower molecular weight PAHs as follows: PAH3 degraded into PAH2 degraded into PAH1 degraded out of the system. Results of this analysis are shown in Figure 3-63, in which the calibrated loads scenario was run with first-order degradation only (*2xloadsWG*) and with PAH group interactions simulated (*2xloadsWG w/yield*). Results indicate that there is not much change in the distribution or mass of PAH2 (Figure 3-63b) or PAH3 (Figure 3-63c) in the system. However, there is a significant increase in PAH1 (Figure 3-63a), indicating that some degradation of higher-molecular weight PAHs into PAH1 could explain for the lack of PAH1 estimated by the model.

The sensitivity of the model to first order degradation rates was also investigated. As mentioned, there is a wide range in reported biodegradation rates for individual PAHs. For this reason, the model was run with the degradation rate constant both increased and reduced by a factor of 10. Results of this analysis are provided in Figure 3-64 and indicate that the model is sensitive to changes in the estimated degradation rate. Reducing the degradation rate led to an overestimation of PAH2 (Figure 3-64b) and PAH3 (Figure 3-64c), while increasing the degradation rate led to an underestimation of all PAHs. For PAH1 (Figure 3-56a), reducing the degradation rate by a factor of 10 appears to improve the model fit

to the data. However, due to a lack of information regarding degradation of PAHs, it is unclear if reducing the degradation rate by a factor of 10 is more realistic than incorporating PAH interactions (Figure 3-64a) as both appear to improve the model fit to the data.

Table 3-14. Concentrations Used to Compute PAH Sub-Model Calibration Run Input Loads (ug/L)

Source	PAH1 Orig	Suggested PAH1 Multiplier	PAH1 Draft Final	PAH2 Orig	Suggested PAH2 Multiplier	PAH2 Draft Final	PAH3 Orig	Suggested PAH3 Multiplier	PAH3 Draft Final	Comment
NW Br Base	0.056	x 2.0	0.112	0.193	x 2.0	0.386	0.097	x 2.0	0.194	Concentration computed from 6 samples of Gruessner et al. (1998) 1995-96 data
NW Br Storm	0.607	x 2.0	1.214	3.911	x 2.0	7.822	2.631	x 2.0	5.262	Concentration computed from 4 samples of Gruessner et al. (1998) 1995-96 composite data
NE Br Base	0.054	x 2.0	0.108	0.099	x 2.0	0.198	0.044	x 2.0	0.088	Concentration computed from 6 samples of Gruessner et al. (1998) 1995-96 data
NE Br Storm	0.271	x 2.0	0.542	1.634	x 2.0	3.268	0.945	x 2.0	1.890	Concentration computed from 4 samples of Gruessner et al. (1998) 1995-96 composite data
SSTrib Base	0.055	x 2.0	0.110	0.146	x 2.0	0.292	0.071	x 2.0	0.142	Estimated to be the averaged NE/NW Branches baseflow (Gruessner et al., 1998)
SS Trib Storm	0.439	x 2.0	0.878	2.773	x 2.0	5.545	1.788	x 2.0	3.576	Estimated to be the averaged NE/NW Branches stormflow (Gruessner et al., 1998)
CSO	0.439	x 2.0	0.878	2.773	x 2.0	5.545	1.788	x 2.0	3.576	Estimated to be the averaged NE/NW Branches stormflow (Gruessner et al., 1998)

Table 3-15. WASP Input Parameters for PAH Sub-Model

Process	Parameter	Units	PAH1	PAH2	PAH3	Source
<i>Downstream Boundary Condition:</i>						
	Potomac Boundary Concentration	ug/L	0.05	0.009	0.025	Calibration
<i>Adsorption:</i>						
	K _d for fine-grained sediment	L _w /kg _s	38,176	531,645	2,299,419	Mean K _d based on site- specific baseflow data
	K _d for medium-grained sediment	L _w /kg _s	9,544	132,911	574,855	¼ of mean K _d
<i>First-order Degradation:</i>						
	Water Column Rate constant	per day	1.0E-02	5.0E-03	5.0E-04	Estimated based on reported literature values (Aronson et al., 1999 and Mackay et al., 1992).
	Sediment Rate constant	per day	1.0E-03	5.0E-04	5.0E-05	Estimated based on reported literature values (Aronson et al., 1999 and Mackay et al., 1992).
<i>Volatilization:</i> (Using option 4 – transfer coefficients are computed by WASP assuming a flowing estuary)						
	Molecular Weight	g/mole	154	215	265	average by type from several refs
	Henry's Law Coefficient	atm – m ³ /mole	4.75E-04	1.03E-04	3.15E-06	average by type from several refs
	Atmospheric Concentration	mg/L	1.50E-08	1.30E-09	7.80E-12	(Bamford et al., 1999, Gustafson and Dickhut, 1988)

Table 3-16. Comparison of Washington Gas Annual PAH Load (kg/year) Estimates Based on Average PAH Concentrations in Groundwater and Sediment

	Groundwater Average Concentration (ug/L)	Groundwater Est. Load ¹ (kg/year)	Average Sediment Concentration ² (ug/L)	Pore Water Diffusion Est. Load ² (kg/year)
PAH1	2361.2	54.80	44029	9.48
PAH2	201.2	4.67	47019	10.12
PAH3	56.2	1.30 ³	26211	5.64
Total	2618.6	60.78	117258	25.23

¹ Computed from average groundwater concentration and estimated total flow of 16,800 gpd (Hydro-Terra, Inc., 1998).

² Based on sediment concentration data (AWTA/NOAA database).

³ Load is underestimated because several analytes in PAH group 3 were not included in the groundwater analysis.

Table 3-17. Estimated PAH Atmospheric Air Concentrations

	Patapsco River ¹ (mg/L)	Elizabeth River ² (mg/L)	Hampton ² (mg/L)	Overall Average (mg/L)
naphthalene	NA	NA	NA	
2-methyl naphthalene	1.81E-09	NA	NA	
acenaphthylene	1.80E-10	NA	NA	
acenaphthene	2.00E-10	NA	NA	
fluorene	1.60E-09	6.62E-09	1.71E-08	
phenanthrene	7.80E-09	1.47E-08	4.48E-08	
Sum PAH Group 1	1.39E-08	6.40E-08	1.86E-07	8.8E-08
fluoranthene	1.50E-09	2.51E-09	4.94E-09	
pyrene	1.10E-09	1.58E-09	1.99E-09	
benz[a]anthracene	NA	7.46E-11	1.51E-11	
chrysene	4.00E-11	3.62E-10	9.91E-11	
Sum PAH Group 2	3.52E-09	4.52E-09	7.05E-09	5.0E-09
benzo[k]fluoranthene	NA	6.72E-12	4.68E-12	
benzo[a]pyrene	NA	2.10E-11	3.12E-12	
perylene	NA	NA	NA	
indeno[1,2,3-c,d]pyrene	NA	6.06E-12	8.55E-12	
benzo[g,h,i]perylene	NA	9.77E-12	ND	
dibenz[a,h+ac]anthracene	NA	9.34E-12	4.02E-12	
Sum PAH Group 3	NA	6.34E-11	2.55E-11	4.4E-11

NA = not analyzed

ND = not detected

¹ Bamford et al., 1999² Gustafson and Dickhut, 1997**Table 3-18. Estimated Annual Atmospheric Deposition of Total PAHs to the Anacostia River (kg/year)**

Chesapeake Bay - Regional ¹		Chesapeake Bay - Urban ¹		Baltimore ²	
Wet Deposition	Dry Deposition	Wet Deposition	Dry Deposition	Wet Deposition	Dry Deposition
0.10 - 0.15	0.07 - 0.11	0.41 - 0.61	0.28 - 0.42	1.36 - 2.44	0.36 - 0.57

Calculations assume that the surface area of the Anacostia River is 3,300,300 m² and are based on data adapted from:

¹CBP (1999) and² Offenberg and Baker (1999)

Table 3-19. Average Annual Load Contributions and Losses by Source, for Calibrated PAH Sub-Model

	PAH1		PAH2		PAH3	
	kg	% ²	kg	%	kg	%
Upstream	34.4	55.3	203.7	62.5	127.9	62.3
SS Tribs	5.6	9.0	33.4	10.3	21.3	10.4
LBD	9.2	14.7	57.3	17.6	36.9	18.0
Watts	1.4	2.2	8.2	2.5	5.2	2.5
CSOs	2.2	3.6	13.2	4.0	8.4	4.1
Wash Gas Load	9.5	15.2	10.1	3.1	5.6	2.7
Total Input ¹	62.2	100	325.9	100	205.4	100
Export to Potomac	-16.6	-26.7	-104.0	-31.9	-66.9	-32.6
Kinetic Losses	-38.8	-62.3	127.1	-39.0	-11.3	-5.5

¹ Total Input is the sum of loads from upstream, SS Tribs, LBD, Watts and CSOs.

² % represents the percentage of total input (sum of all loads).

Table 3-20. Comparison of Average Annual PAH Kinetic Losses (kg/year)

With Calibrated Loads	PAH1	PAH2	PAH3
Without WG ¹	-3.4	-8.0	-1.5
With WG	-38.8	-127.1	-11.3
With WG no degradation (volatilization only)	-11.51	-4.69	-0.05
With WG no volatilization (degradation only)	-32.4	-124.3	-11.2

¹ WG = Washington Gas

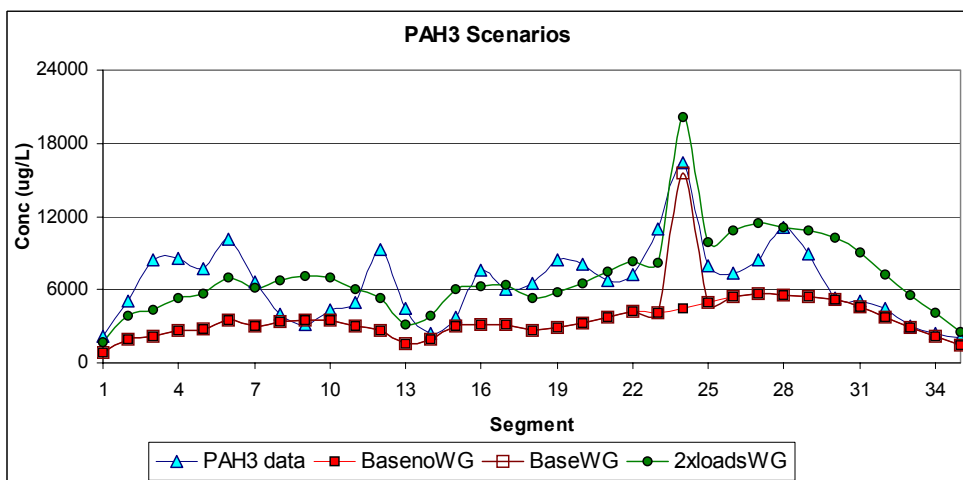
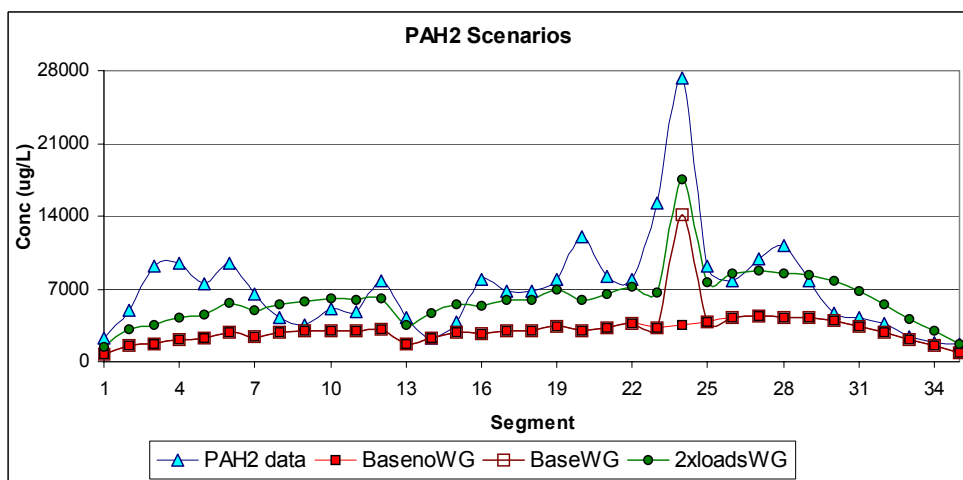
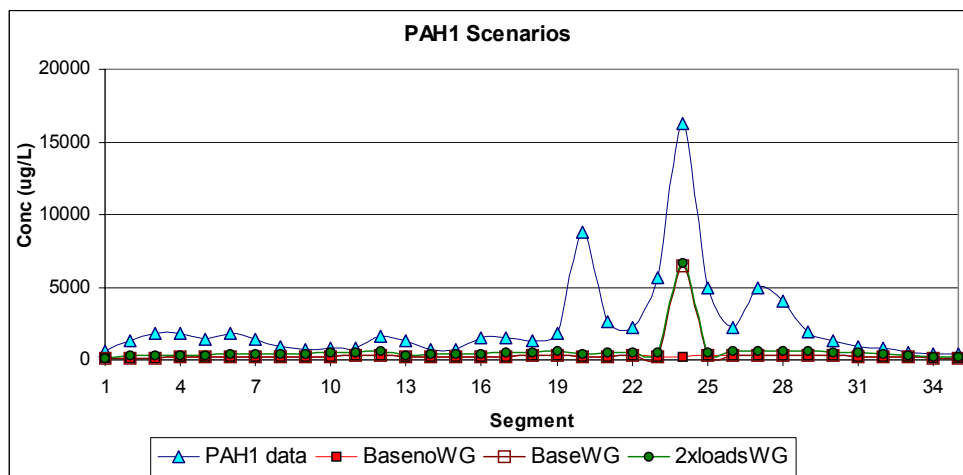


Figure 3-57. PAH Bed Sediment Results: Last day of 6-year run for base scenario (*BasenoWG*), base loading with Washington Gas loads (*BaseWG*), and with upstream and downstream loading doubled (*2xLoads WG*)

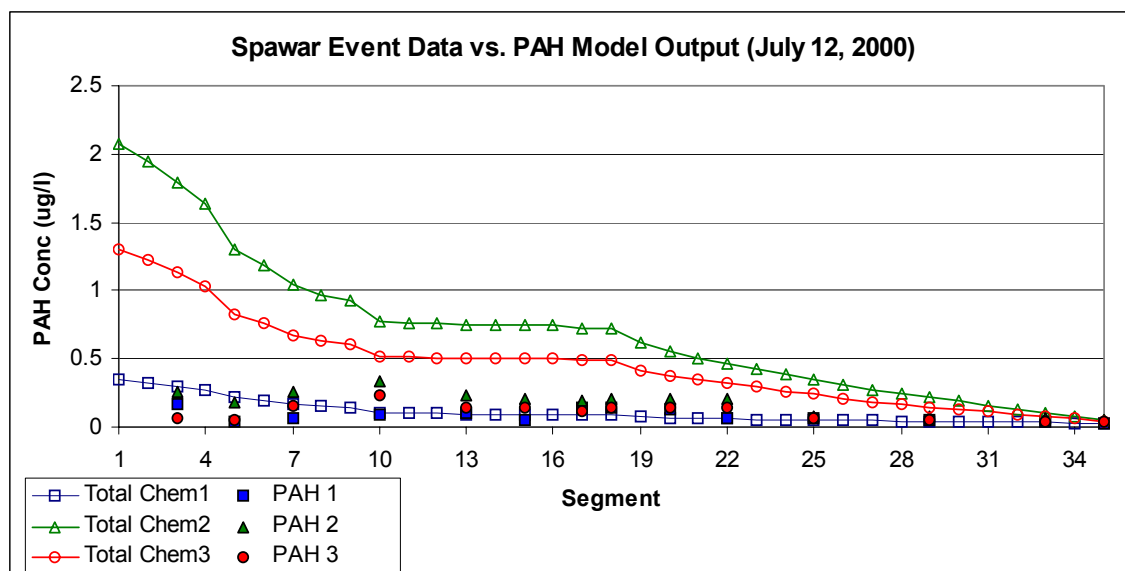


Figure 3-58. Predicted vs. Measured Water Column Concentrations of PAHs, Based on Katz et al. (2000) Single Event Data

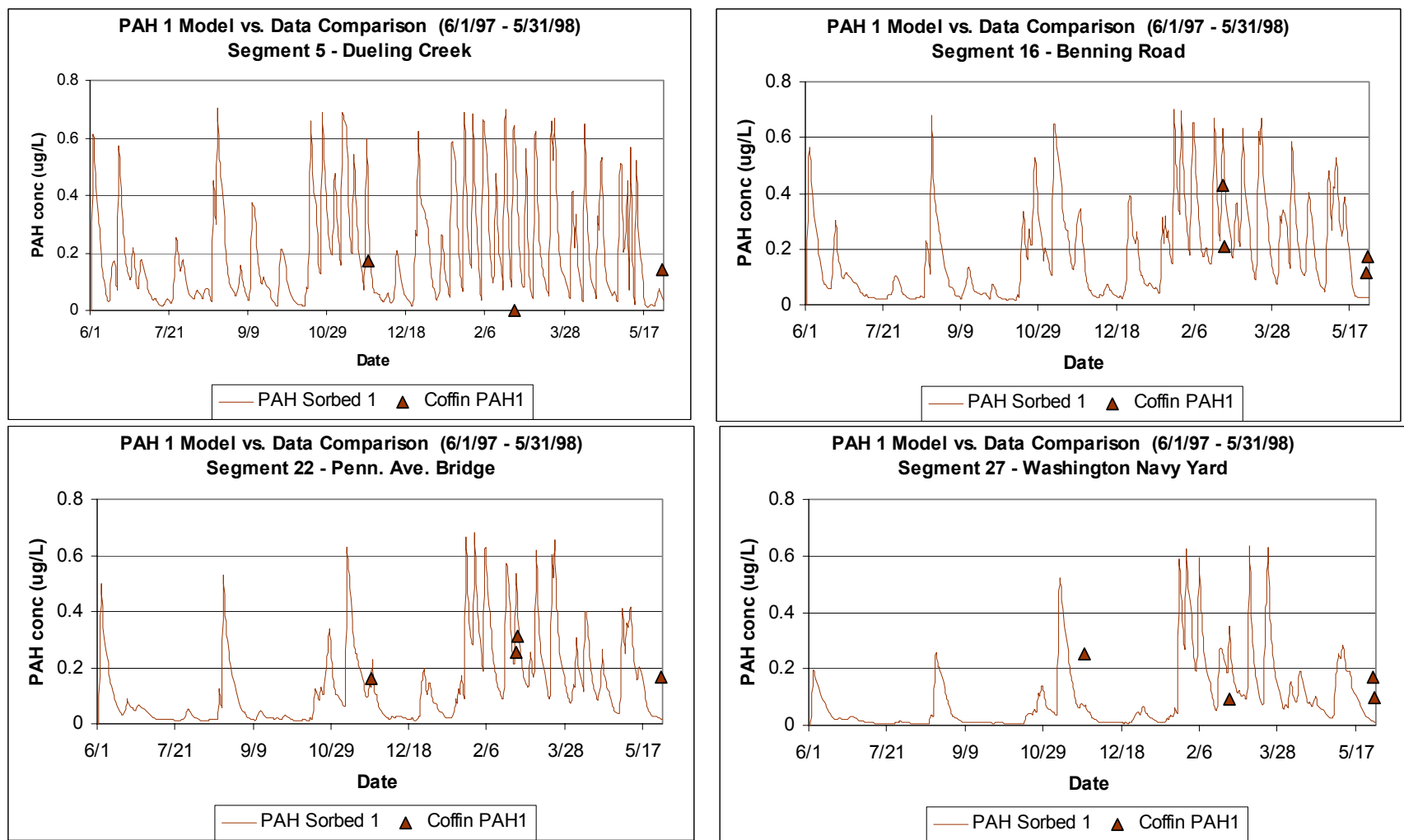


Figure 3-59. PAH1 Water Column Results, Based on Coffin et al. (1998) Data.

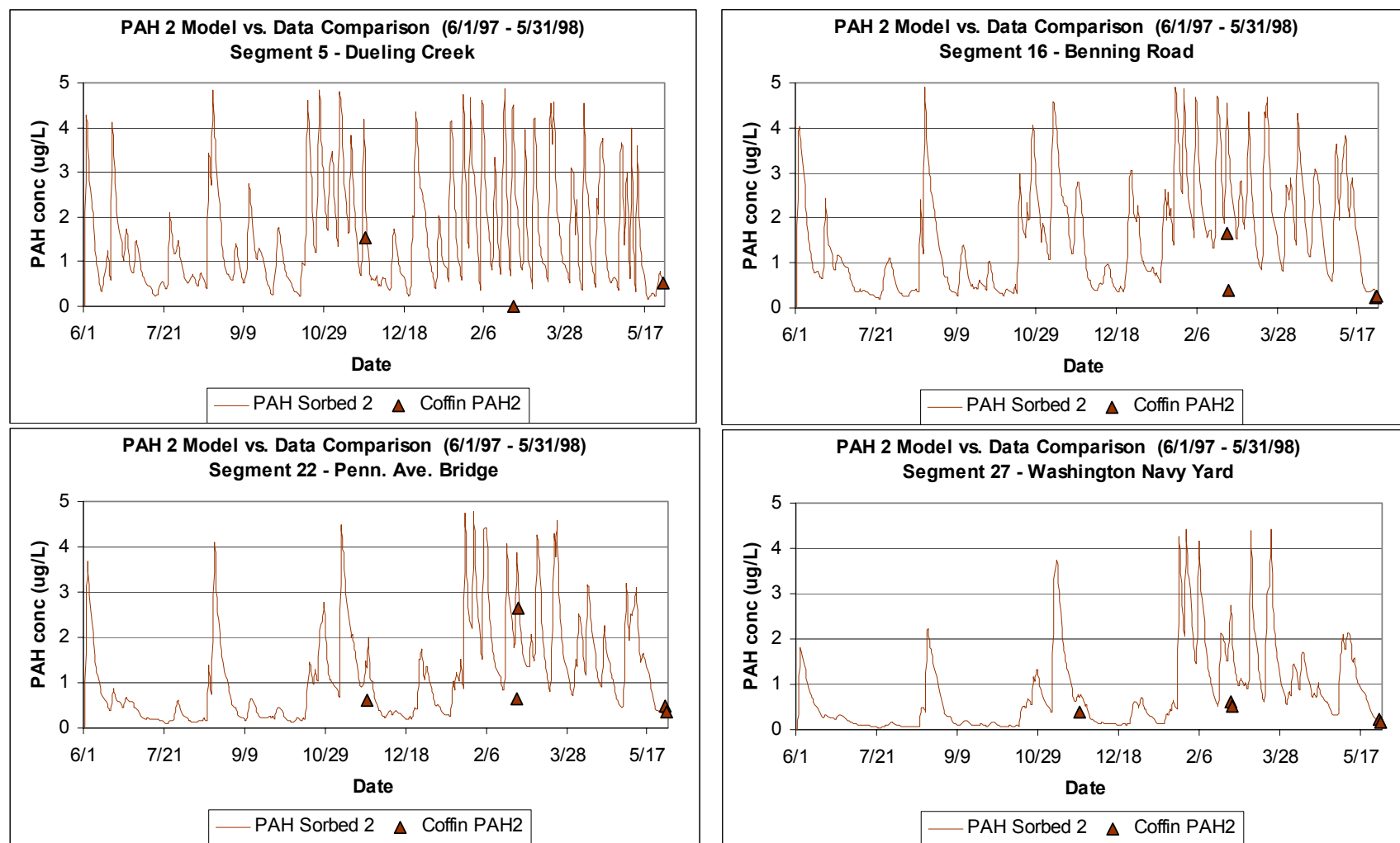


Figure 3-60. PAH2 Water Column Results - Based on Coffin et al. (1998) Data.

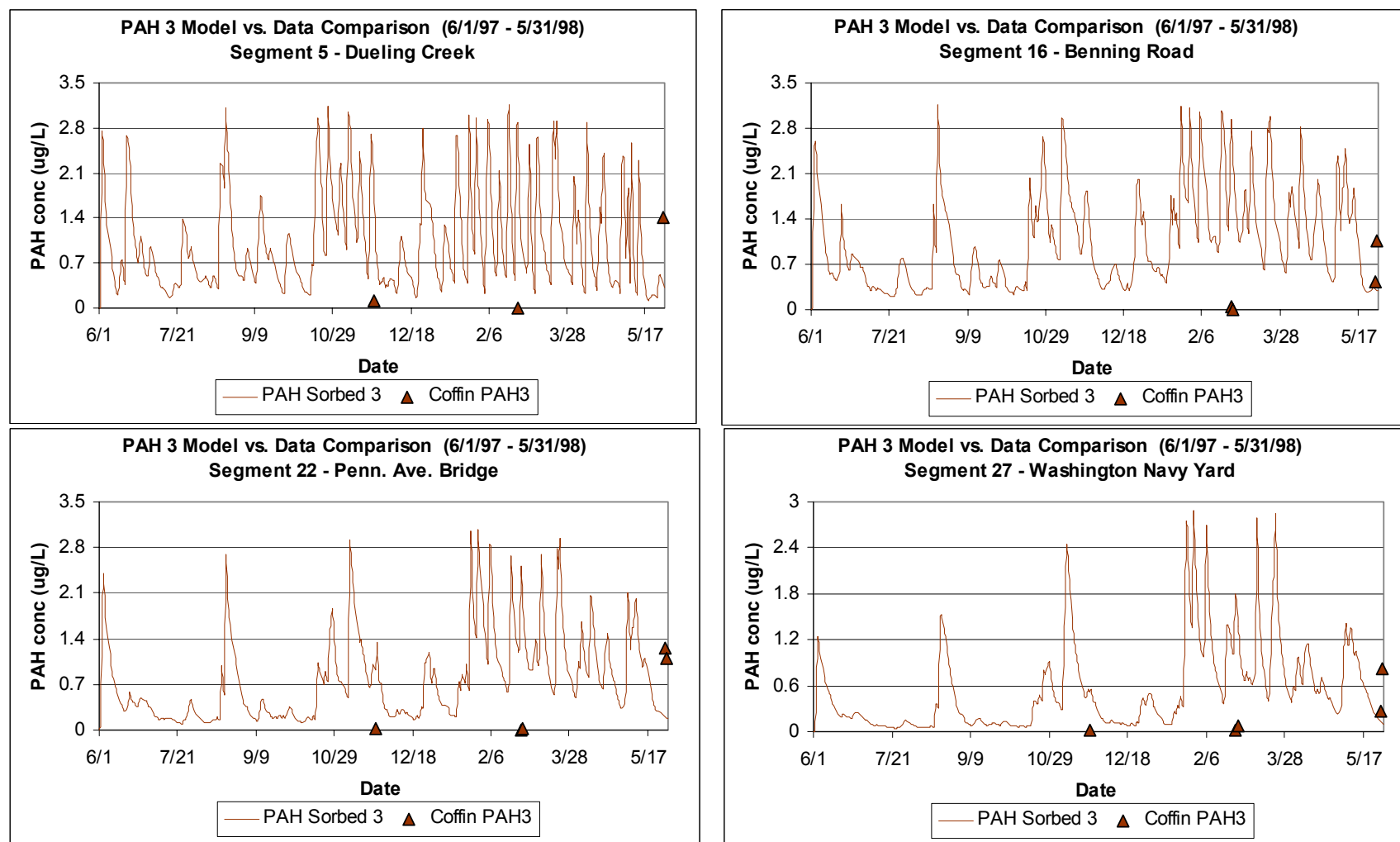


Figure 3-61. PAH3 Water Column Results - Based on Coffin et al. (1998) Data.

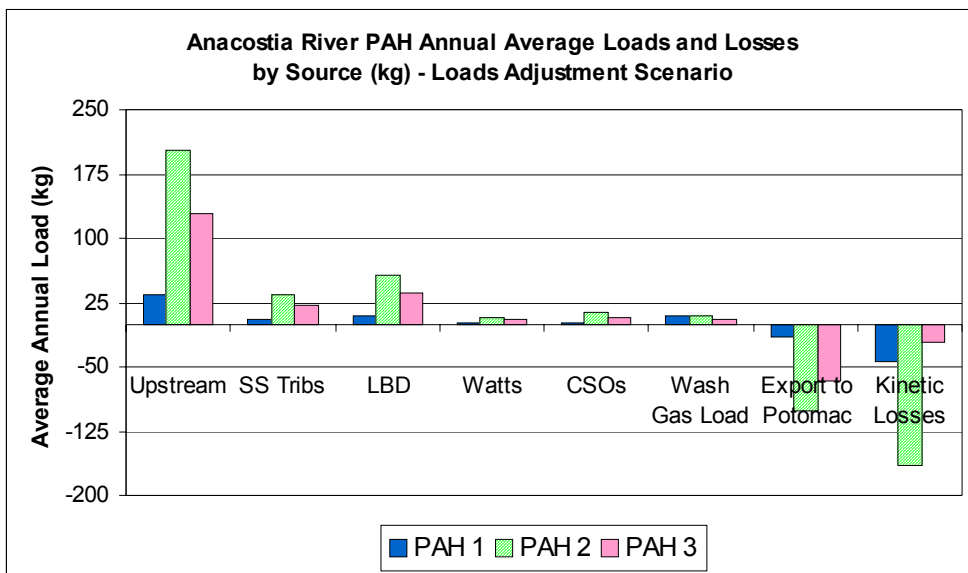


Figure 3-62. Summary of Average Annual Loads and Losses for the Calibrated PAH Sub-Model

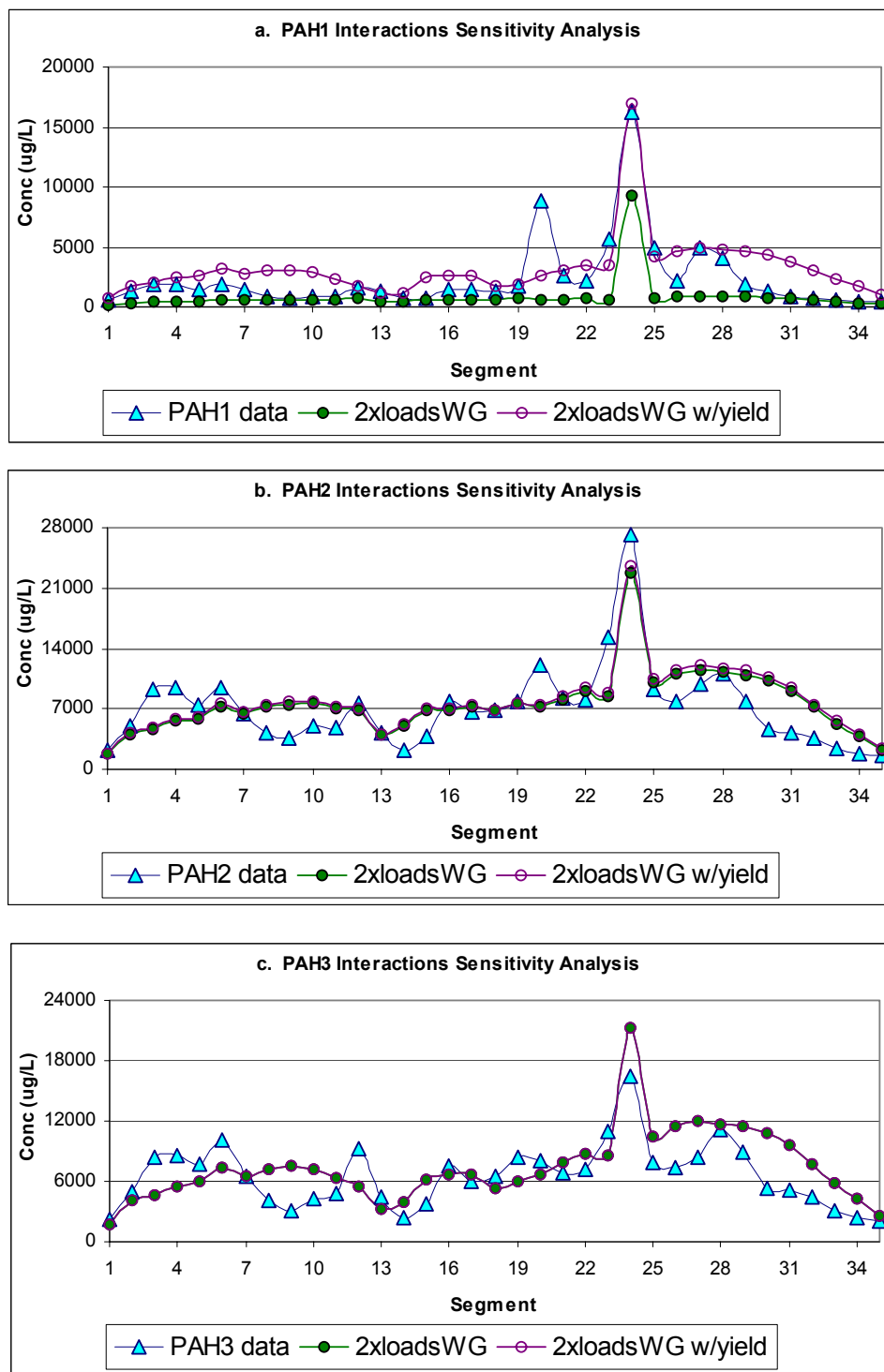


Figure 3-63. PAH Interactions Sensitivity Analysis in which PAH3 Degraded into PAH2 which Degraded into PAH1 which Degraded Out of the System

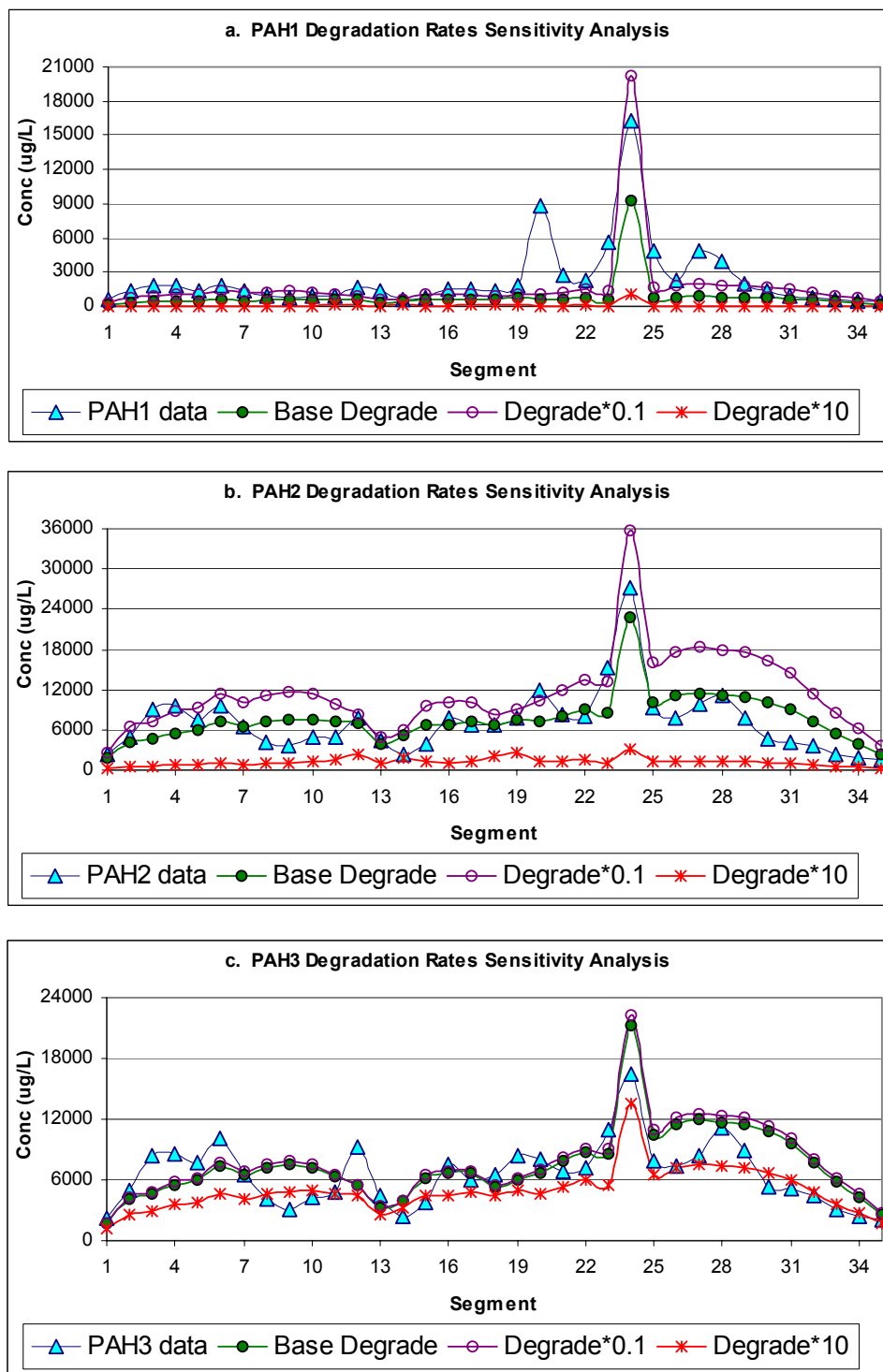


Figure 3-64. PAH Degradation Rate Sensitivity Analysis

3.3.5. Chlordane and Heptachlor Epoxide (PEST1) Sub-Model

Model Description

The TAM/WASP sub-model PEST1 has been set up to simulate total chlordane (comprised of cis-chlordane, trans-nonachlor, and oxychlordane) and heptachlor epoxide (Table 1-2). Transport and fate processes simulated include advection and dispersion, absorption to the medium- and fine-grained sediment fractions, and volatilization. ICPRB feels that this simple modeling framework is appropriate, given that water column calibration data for total chlordane and heptachlor epoxide were not available for the tidal portion of the Anacostia River.

Input Parameters

Estimated baseflow and stormflow concentrations are given in Table 3-21 for total chlordane (Chem1) and heptachlor epoxide (Chem2). NE and NW Branch values are means, assuming log normal distributions, of data collected by Gruessner in 1995 and 1996 (Gruessner et al., 1998). Tidal sub-basin storm, separate storm sewer (SS) system, and combined sewer overflows (CSO) values are estimates because stormwater monitoring data for the tidal portion of the Anacostia River were not available and DC MS4 results are all non-detect. Therefore, the values are derived by averaging upstream concentrations. Tidal sub-basin tributary baseflow concentrations are estimated based on the NE/NW Branches baseflow results.

Input parameters for downstream boundary conditions, adsorption, and volatilization are given in Table 3-22. The boundary concentrations for total chlordane and heptachlor epoxide at the confluence with the Potomac River are calibrated to 0.00015 ug/L and 0.000002 ug/L respectively because water column data was not available for this location. As ICPRB so far has been unable to find atmospheric concentrations for total chlordane and heptachlor epoxide for the Washington/Baltimore area, average air concentrations are estimates based on data reported by Jantunen et al. (2000) for Alabama.

Model Results

A comparison of model predictions (last day of 6 year run) versus bed sediment concentration data suggests that the model accounts reasonably well for mass inputs of total chlordane into the tidal portion of the Anacostia River (Figure 3-65). The model suggests that volatilization may not be an important fate process for chlordane as the model outputs without volatilization (Figure 3-65) and with volatilization (Figure 3-66) are very similar. A mass balance for total chlordane loads by source, kinetic losses, and net export to the Potomac River is shown in Figure 3-67. The relative contribution of the sources and losses compared to total river input (sum of all loads) is provided in Table 3-23. Based on the mass balance analysis, it appears that upstream loadings account for most of the total chlordane load to the Anacostia River.

A comparison of model predictions versus bed sediment concentration data for heptachlor epoxide shows that the model predicted bed sediment concentrations are too high (Figure 3-68), even when the input concentrations are lowered by 30% (Figure 3-69). Model predictions, however, improve when volatilization is included as a fate process (Figure 3-70). Based on these calibration results, ICPRB recommends using volatilization and a 30% load reduction, which is within a typical 90% confidence interval based on ICPRB upstream load uncertainty analyses for a number of constituents. A mass

balance for the loads adjusted scenario, which also includes volatilization, is shown in Figure 3-68 for heptachlor epoxide, and the relative contribution of the sources and losses compared to the total river load is provided in Table 3-23. It appears that upstream inputs are the primary course of heptachlor epoxide to the Anacostia River.

Model predictions of water column concentrations cannot be compared to measured water column concentrations, as water column data for total chlordane and heptachlor epoxide were not available.

Table 3-21 Concentrations Used to Compute PEST1 Sub-Model Calibration Run Input Loads (ug/L)

Source	Chem1 Original	Suggested Multiplier	Chem1 Final	Chem2 Original	Suggested Multiplier	Chem2 Final	Comment
NW Br Base	0.001186	x 1	0.001186	0.001211	x 0.7	0.000848	Concentration computed from 6 samples of Gruessner et al. (1998) 1995-96 data
NW Br Storm	0.018928	x 1	0.018928	0.001456	x 0.7	0.001019	Concentration computed from 4 samples of Gruessner et al. (1998) 1995-96 data
NE Br Base	0.000813	x 1	0.000813	0.000719	x 0.7	0.000503	Concentration computed from 6 samples of Gruessner et al. (1998) 1995-96 data
NE Br Storm	0.003751	x 1	0.003751	0.001314	x 0.7	0.00092	Concentration computed from 4 samples of Gruessner et al. (1998) 1995-96 data
SSTrib Base	0.000963	x 1	0.000963	0.000916	x 0.7	0.000641	Estimated to be the averaged NE/NW Branches baseflow (Gruessner et al., 1998)
SS Trib Storm	0.009829	x 1	0.009829	0.001367	x 0.7	0.000957	Estimated to be the averaged NE/NW Branches stormflow (Gruessner et al., 1998)
CSO	0.009829	x 1	0.009829	0.001367	x 0.7	0.000957	Estimated to be the averaged NE/NW Branches stormflow (Gruessner et al., 1998)

Table 3-22. WASP Input Parameters for PEST1 Sub-Model

Process	Parameter	Units	CHEM1	CHEM2	Source
<i>Downstream Boundary Condition:</i>					
	Potomac Boundary Concentration	ug/L	0.00015	0.000002	Calibration
<i>Adsorption:</i>					
	K _d for fine-grained sediment	L _w /kg _s	83,600	8,300	K _d based on site- specific baseflow data (Gruessner et al., 1998)
	K _d for medium-grained sediment	L _w /kg _s	20,900	2,075	Taken to be ¼ of the fine-grained sediment K _d . Based on best professional judgment.
<i>Volatilization:</i> (Using option 4 – transfer coefficients are computed by WASP assuming a flowing estuary)					
	Molecular Weight	g/mole	430 (Estimated to reflect group)	389	
	Henry's Law Coefficient	atm – m ³ /mole	2.9E-04	3.2E-05	ATSDR
	Atmospheric Concentration	mg/L	5.45E-11	1.6E-11	Mean concentration in Alabama (based on Jantunen et al., 2000)

Table 3-23. Average Annual Load Contributions and Losses by Source for the Calibrated PEST1 Sub-Model

Loads / Losses	Total Chlordane		Heptachlor Epoxide	
	kg	%²	kg	%
Upstream	0.417	67.3	0.056	69.2
SS Tribs	0.061	9.9	0.009	10.5
LBD	0.102	16.5	0.011	13.3
Watts	0.015	2.4	0.002	2.5
CSOs	0.024	3.9	0.004	4.4
Total Input ¹	0.619	100	0.082	100
Kinetic Losses	-0.054	-8.7	-0.012	-15.1
Export to Potomac	-0.242	-39.0	-0.048	-59.9

¹ Total Input is the sum of loads from upstream, SS Tribs, LBD, Watts and CSOs.

² % represents the percentage of total input (sum of all loads).

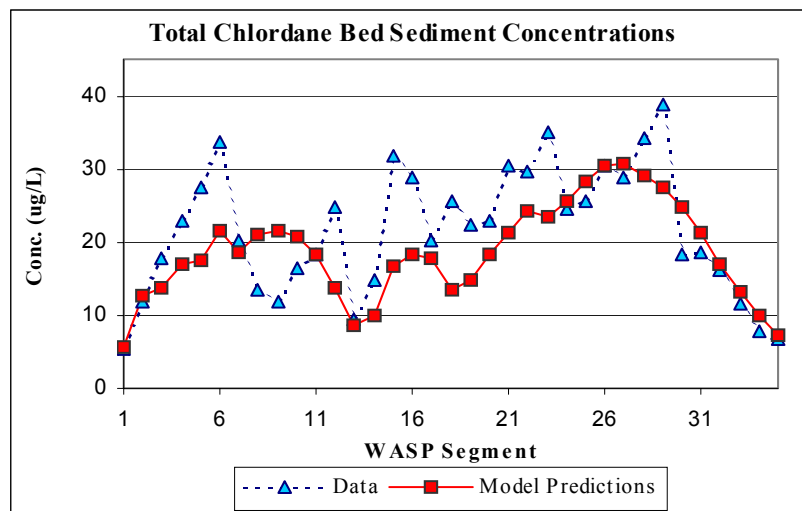


Figure 3-65. Total Chlordane Bed Sediment Concentration: Model predictions without volatilization

Figure 3-66. Total Chlordane Bed Sediment Concentration: Model predictions with volatilization

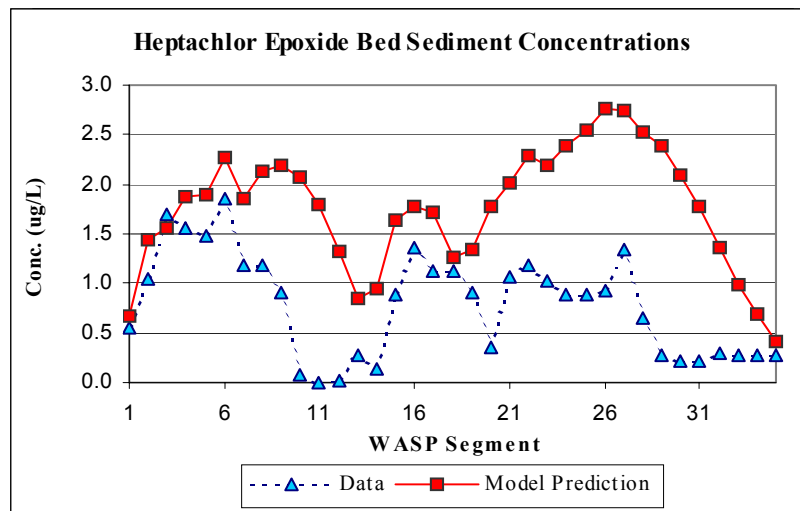


Figure 3-67. Heptachlor Epoxide Bed Sediment Concentration: Base Scenario

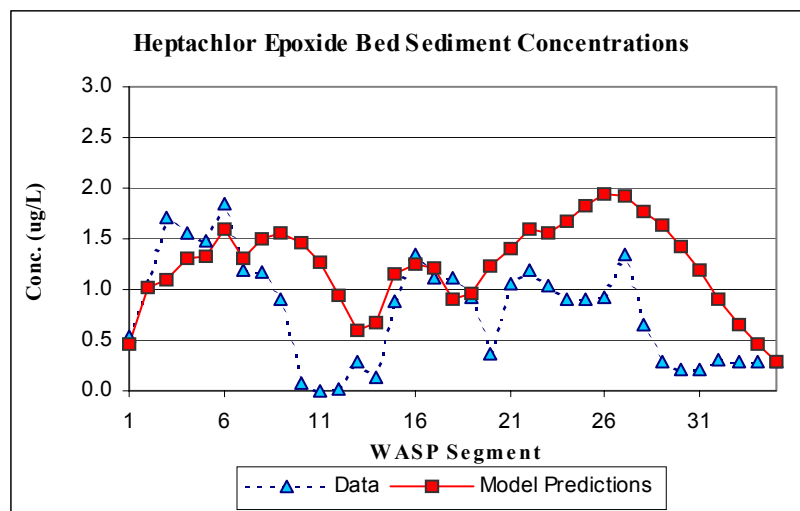


Figure 3-68. Heptachlor Epoxide Bed Sediment Concentration: Model predictions with 30% load reduction

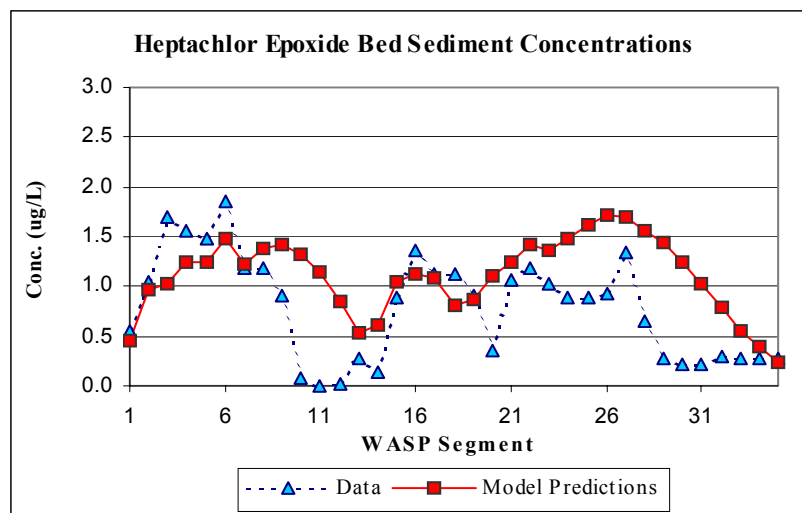


Figure 3-69. Heptachlor Epoxide Bed Sediment Concentration: Model predictions with volatilization and 30% load reduction

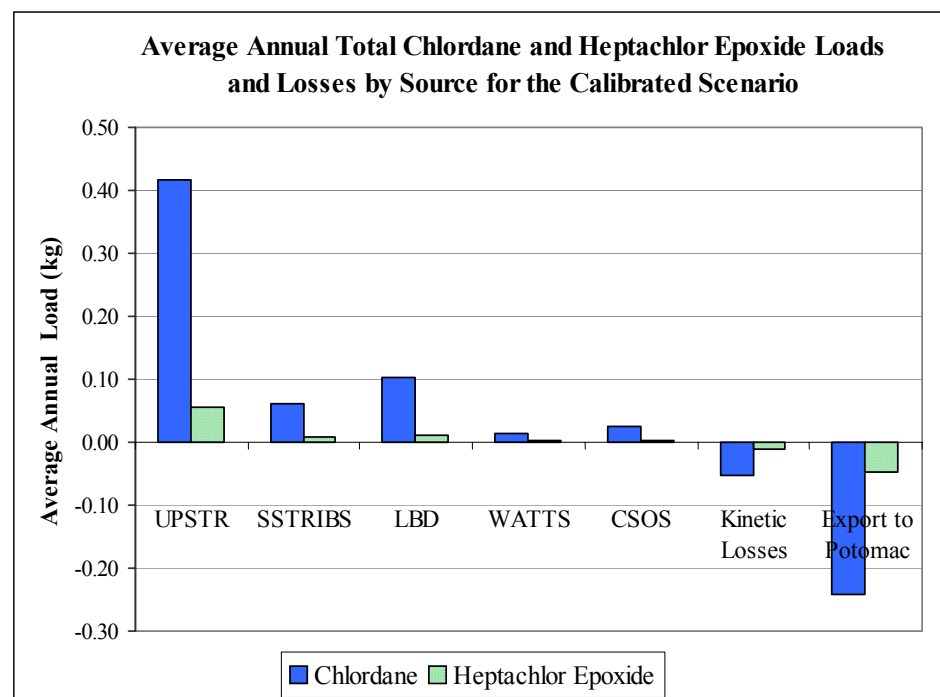


Figure 3-70. Summary of Average Annual Loads and Losses for the Calibrated Chlordane and Heptachlor Epoxide (PEST1) Sub-Model

3.3.6. Dieldrin (PEST2) Sub-Model

Fate Processes

Probable fate processes for dieldrin, as listed in the US Army Corps of Engineers' Riverine Emergency Management Model, include sorption, volatilization, photolysis, and bioaccumulation (U.S. ACE 1997). Although volatilization from water surfaces can be expected based on a Henry's Law coefficient of 5.2×10^{-6} atm-m³/mole, this fate process may be attenuated by adsorption to suspended solids and sediment (ATSDR 2000). Furthermore, data on volatilization rates are conflicting, with half-lives ranging from hours to months (Spectrum Laboratories). Based on a vapor pressure of 5.89×10^{-6} mm Hg at 25 °C, dieldrin may exist in both the vapor and particulate phases in the atmosphere, where it is degraded by hydroxyl radicals, with an estimated half-life of 42 hours (TOXNET). Particulate phase dieldrin, however, is more stable and may be transport great distances through the air to be later removed by wet and dry deposition (ATSDR 2000).

Dieldrin may rearrange via photolysis into its stereoisomer photodieldrin, with a reported half-life of about four month (Spectrum Laboratories). "It is unlikely, however, that photodieldrin occurs widely in the environment" (ATSDR 2000). In an aquatic environment, dieldrin does not biodegrade and undergoes hydrolysis only slowly, with a half-life of greater than four years (TOXNET).

Dieldrin is highly persistent in soil with a 95% disappearance rate of 5 to 25 years depending on soil type, and its adsorptive capacity to different soil types has been reported as organic soil > sediment > sandy loam > sand (Cornell).

Model Description

Based on the above description of likely fate processes, a TAM/WASP model, referred to as the PEST2 Model (Table 1-2), has been set up for dieldrin. Transport and fate processes simulated include advection and dispersion, absorption to the medium-grained and fine-grained sediment fractions, and volatilization.

Wet and dry deposition has not been included in the model because regional data has not been found, although concentration data for stations in the Great Lakes region is available from the Integrated Atmospheric Deposition Network (IADN). However based on our experience with other chemicals, it is unlikely that wet and dry deposition contributes significant loads due to the relative small surface area of the tidal river.

Aldrin has been found in a few of the historical sediment sample data sets (AWTA/NOAA database: 1995 PEPCO and 1997 Sediment Core Analysis). Aldrin could be viewed as a source for dieldrin because it reportedly degrades readily into dieldrin in aerobic, biologically active soils and under anaerobic conditions in aquatic environments (TOXNET), although the exact pathways for these reactions are not clear. In water, photodieldrin may be formed via photolysis from aldrin (ATSDR 2000). It is questionable, however, whether this is a likely process in the Anacostia River, as photolysis takes place near the water surface, and aldrin has only been found once, as particulate in a storm sample, in Anacostia River water column data. Because aldrin was below the detection limit in all NE/NW Branches monitoring data and all sediment samples in the Velinsky and Ashley 2001 data

set, it appears that it does not play an important role in determining dieldrin concentrations in the Anacostia and therefore, was not included as a constituent in the dieldrin model.

Input Parameters

Estimated baseflow and stormflow concentrations used for the load estimates can be found in Table 3-24. NE and NW Branch values are means, assuming log normal distributions, of data collected by Gruessner in 1995 and 1996 (Gruessner et al., 1998). Tidal sub-basin tributaries and separate storm sewer (SS) system concentrations are estimated at 0.00029 ug/L, based on MS4 monitoring data (Nicoline Shelterbrandt, private communication) of 20 samples with 18 non-detects, where non-detects were estimated $\frac{1}{2}$ the detection limit (Table 2-5). Tidal sub-basin tributary baseflow concentrations are estimated to be 0.000641 ug/L, based on the NE/NW Branches baseflow results. NE/NW Branches stormflow concentrations and combined sewer system overflows (CSOs) concentrations are estimated to be 0.00029 ug/L, based on the MS4 monitoring results.

Proposed input parameters for downstream boundary conditions, adsorption, and volatilization are listed in Table 3-25. Because ICPRB has so far been unable to find atmospheric concentrations of dieldrin in the Washington/Baltimore area, the mean air concentration of dieldrin reported by Jantunen et al. (2000) for Alabama is used in the model.

Model Results

A comparison of the model prediction (last day of six year run) versus bed sediment concentration averages suggests that the model accounts reasonably well for dieldrin mass inputs into the tidal portion of the Anacostia River as shown in Figure 3-71. A mass balance analysis for dieldrin loads by source, kinetic losses, and net export to the Potomac River is shown in Figure 3-72. The relative contribution of the sources and losses compared to the total river load is provided in Table 3-26. It appears that upstream loadings are the primary sources of dieldrin to the Anacostia River.

Model predictions of water column concentrations cannot be compared to measured water column concentrations because water column data for dieldrin were not available.

Sensitivity Runs

Sensitivity runs were made to investigate the effects of changes in downstream boundary conditions. Model runs with downstream boundary concentrations set at 5.0×10^{-6} ug/L and 5.0×10^{-4} ug/L, as shown in Figures 3-73 and 3-74 respectively, demonstrate that the model is not very sensitive to decreases in the downstream boundary concentration. However, a downstream boundary condition of 5.0×10^{-4} ug/L, comparable to dieldrin concentrations in baseflow Northeast and Northwest Branch data (see Table 2-4), does not produce a good match to bed sediment dieldrin concentration data.

Table 3-24. Concentrations Used to Compute PEST2 Sub-Model Calibration Run Input Loads (ug/L)

Source	Chem1 Original	Suggested Multiplier	Chem1 Final	Data Source/Comment
NW Br Base	0.000784	x 1	0.000784	Gruessner et al.1998 data, 6 samples
NW Br Storm	0.001697	x 1	0.001697	Gruessner et al., 1998 composite data, 4 samples
NE Br Base	0.000546	x 1	0.000546	Gruessner et al.1998 data, 6 samples
NE Br Storm	0.000650	x 1	0.000650	Gruessner et al., 1998 composite data, 4 samples
SSTrib Base	0.000641	x 1	0.000641	Estimated to be the averaged NE/NW Branches baseflow (Gruessner et al., 1998)
SS Trib Storm	0.00029	x 1	0.00029	DC MS4 monitoring data, 20 samples with 18 NDs
CSO	0.00029	x 1	0.00029	Assuming DC MS4 value

Table 3-25. WASP Input Parameters for PEST2 Sub-Model

Process	Parameter	Units	CHEM1	Source/Comments
Downstream Boundary Condition:				
	Potomac boundary concentration	ug/L	5.0E-5	Bed sediment calibration
Adsorption:				
	K _d for fine-grained sediment	L _w /kg _s	24,700	Based on 1998 water column data (Velinsky et al.)
	K _d for medium-grained sediment	L _w /kg _s	6,175	Taken to be ¼ of the fine-grained sediment K _d based on best professional judgment
Volatilization:				
	Molecular Weight	g/mole	381	
	Henry's Law Coefficient ^a	atm – m ³ /mole	5.2E-06	ATSDR
	Atmospheric Concentration	mg/L	3.8E-11	Mean concentration in Alabama (Jantunen et al. 2000)

^a Literature values of Henry's law coefficient for dieldrin range from 5.2E-06 (ATSDR 2000) to 1.51E-05 (U.S. EPA 1996).

Table 3-26. Average Annual Load Contributions and Losses by Source for Calibrated Metals² Sub-Model

	Dieldrin	
	kg	%²
Upstream	0.059	83.5
SS Tribs	0.005	6.6
LBD	0.004	5.5
Watts	0.001	1.5
CSOs	0.002	2.9
Total Input ¹	0.071	100
Kinetic Losses	-0.001	-0.9
Export to Potomac	-0.029	-40.8

¹ Total Input is the sum of loads from upstream, SS Tribs, LBD, Watts and CSOs.

² % represents the percentage of total input (sum of all loads).

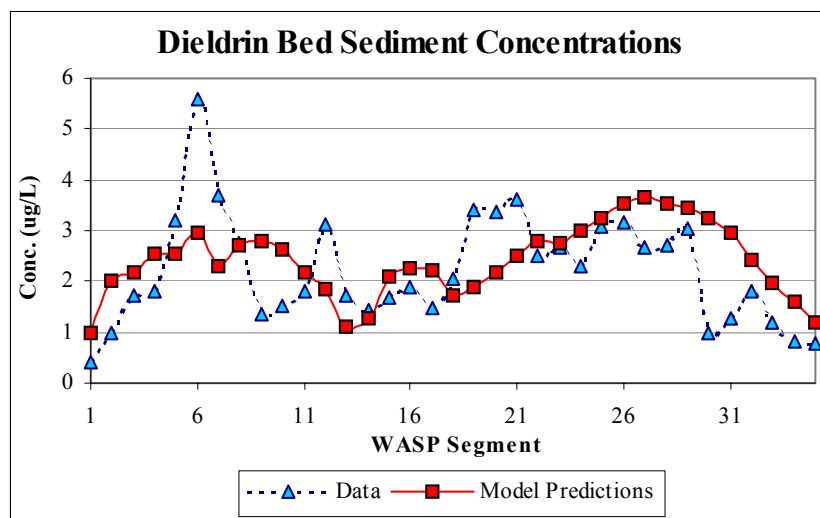


Figure 3-71. Dieldrin Bed Sediment Results for Calibrated Model

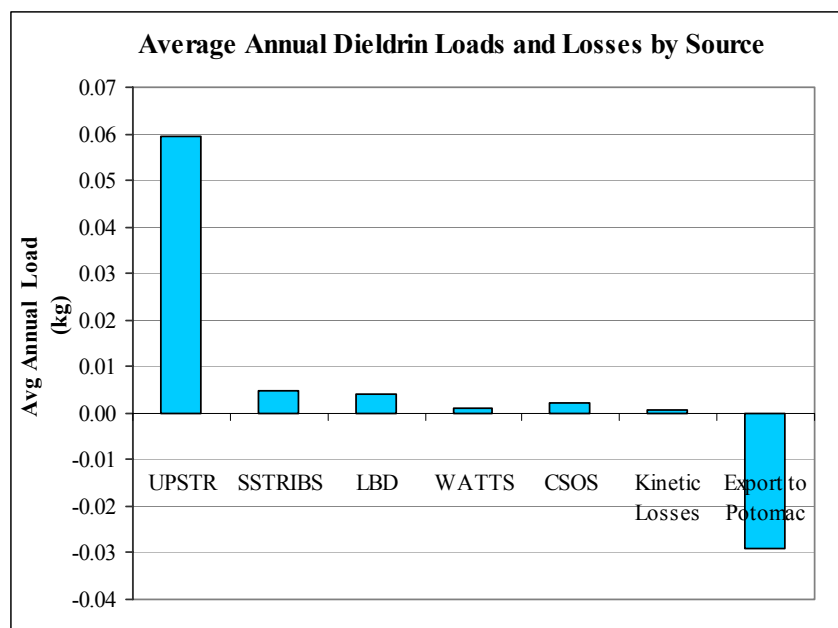


Figure 3-72. Summary of Average Annual Loads and Losses for the Calibrated Dieldrin (PEST2) Sub-Model

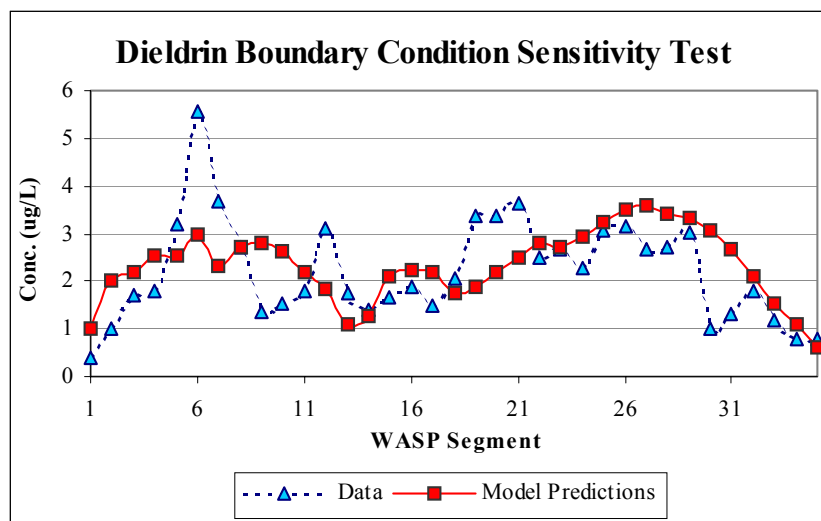


Figure 3-73. Dieldrin Bed Sediment Results - Potomac Boundary Condition at 5×10^{-6} ug/L

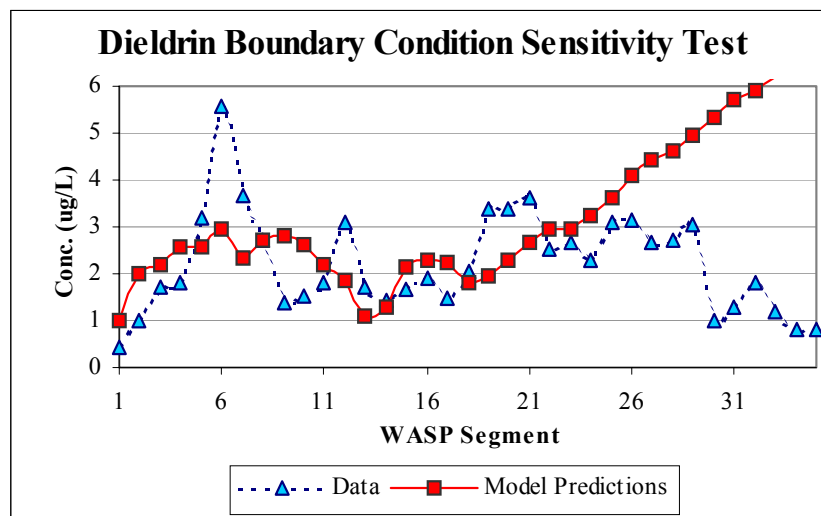


Figure 3-74. Dieldrin Bed Sediment Results - Potomac Boundary Condition at 5×10^{-4} ug/L

3.3.7. DDT Sub-Model

Model Description

The TAM/WASP DDT model simulates the fate and transport of the following three DDT isomers/metabolites: p,p DDD, p,p DDE, and p,p DDT (Table 1-2). The decision to model these three constituents was based on data availability. The only fate and transport process simulated, in addition to advection and dispersion, is absorption to the medium and fine-grained sediment fractions.

Volatilization is not included in the kinetic transport of DDT in the model due to a lack of data.

Furthermore, although volatilization from water surfaces can be expected, this fate process is severely attenuated by adsorption to suspended solids and sediment. For example, the DDT volatilization half-life from a model pond is about 129 years when adsorption is considered (TOXNET). The US Army Corps of Engineers' Riverine Emergency Management Model and TOXNET lists other kinetic processes such as photolysis and biodegradation as "probably not important" and were not incorporated into the model framework (TOXNET, U.S. ACE 1997).

Biotransformation is considered a significant fate process for DDTs (TOXNET, U.S. ACE 1997). However, the biotransformation of DDTs is currently not included as a fate process in the model because no data are available to reliably assess the rate of DDT transformation in aquatic environments (TOXNET).

Wet and dry deposition has not been included in the model because regional data has not been found. However, based on our experience with other chemicals, it is unlikely that wet and dry deposition contributes significant loads due to the relative small surface area of the tidal river.

Input Parameters

Estimated baseflow and stormflow concentrations are given in Table 3-27. NE and NW Branch values represent means (assuming log normal distributions) of data collected by Gruessner in 1995 and 1996 (Gruessner et al., 1998). Tidal sub-basin, separate storm sewer (SS) system, and combined sewer overflows (CSO) estimates are based on data from the District's MS4 storm water monitoring program, with an average minimum detection limit of 3E-04 ug/L (Nicoline Shelterbrandt, private communication). Upstream and downstream concentrations used in load computations were increased based on calibration results (Table 3-27), as discussed below. It should be noted that for DDE and DDT, average upstream baseflow concentrations were found to be higher than average stormflow concentrations. Because of the very low concentrations of these constituents and the high numbers of non-detects in the data set (with an average minimum detection limit of 2E-05 ug/L), it is not clear if this result is meaningful, indicating that ground water may be a significant source of DDTs to the system, or if the result is merely due to high variability and uncertainty in reported values. Also, in Table 3-27, note that the estimated load of DDE from the northwest branch is zero for both baseflow and stormflow conditions. This is because DDE was listed as "ND" (not detected) in all samples analyzed from the northwest branch in the Gruessner data set. ICPRB assigned a value of zero to all ND notations based on private communication with David Velinsky.

Bed sediment concentrations of DDTs in the tidal sub-basin are based on the Velinsky and Ashley (2001) data set and several historical data sets available in the AWT/NOAA database, yielding 187, 168, and 185 stations for p,p DDD, p,p DDE, and p,p DDT respectively.

Proposed input parameters for downstream boundary conditions and adsorption are provided in Table 3-28. Model boundary conditions at the Potomac confluence, also given in Table 3-28, were set for p,p DDE and p,p DDT using the results of one pre-storm Potomac river sampling reported in the Velinsky et al. (1999) water column data set. Boundary conditions for p,p DDD were set through calibration as p,p DDD was not analyzed in the Velinsky et al. (1999) study.

Proposed distribution coefficients are also shown in Table 3-28. These values are based on an analysis of water column data available in Velinsky et al. (1999) for p,p DDE and p,p DDT and site-specific NE/NW branches baseflow data for p,p DDD.

Model Results

The DDT model was run for 2 scenarios: a base scenario using calculated loads (Table 3-27) and a scenario in which loads were adjusted to calibrate to sediment data. A comparison of model predictions (last day of 6-year run) versus bed sediment concentration data is presented for each chemical and scenario in Figure 3-75. Model predictions of water column concentrations (total and dissolved) for p,p DDE and p,p DDT were compared to measured water column concentrations based on Velinsky et al. (1999). Results of water column comparisons are shown in Figures 3-76 - 3-79. The predicted water column concentrations based on fish tissue analysis (see section 3.2.2) are also shown in Figures 3-76 to 3-79 for comparison. Total loads by source and net export for the calibration loads adjustment scenario are presented in Figure 3-80. The relative contribution of each source and loss compared to total river input (sum of all loads) is provided in Table 3-29.

Model results for both scenarios suggest that DDT sources of loading to the tidal Anacostia River are currently not well understood (Figure 3-75). In the load adjustment scenario, upstream and downstream loadings of DDTs were altered (multiplication factors presented in Table 3-27) in an effort to calibrate the model (Figure 3-75; *xLoads*). Model results in this scenario account reasonably well for mass inputs of DDT into the tidal portion of the Anacostia River. However, this was accomplished by increasing upstream loads by up to a factor of 4 and downstream loads by up to a factor of 20. Though the load uncertainty analysis in Section 2.5 shows that confidence intervals for mean concentrations may produce this degree of error, it is also possible that important sources of DDTs, particularly downstream, have not been captured by the available data.

Comparison of predicted versus measured water column concentrations for p,p DDE and p,p DDT indicate that calculated loads used in the base scenario account fairly well for water column concentrations of p,p DDE and p,p DDT, as shown in Figures 3-76 and 3-77 respectively. In general, increasing loads by the magnitude necessary to calibrate the sediment layer caused an over-estimation of water column concentrations for p,p DDT (Figures 3-78 and 3-79), and, to a lesser extent, for p,p DDE.

Based on the results of this analysis, it appears that the primary source of p,p DDD in the Anacostia River is due to upstream loading, contributing over 66% of the total load as shown in Table 3-29. Downstream sources contribute the majority of the total load of p,p DDE and p,p DDT. Additional water column data is necessary to further calibrate the model as it appears that there are some sources downstream that have not been captured in the data currently available.

The DDT model calibration results point to the limitations of currently available data and suggest that the sources and loads for DDT may have not yet been well characterized. It should be pointed out that detected concentrations of p,p DDD, p,p DDE, and p,p DDT are some of the lowest found in the studies considered, ranging from just a fraction of a nanogram per liter to approximately one nanogram per liter in water samples (part per trillion). These low concentrations and the corresponding number of non-detects, even for the very precise analytical techniques used by the Gruessner study of Northeast/Northwest Branch loads, suggest that available data is of low precision and accuracy and highly variable.

Table 3-27. Concentrations Used to Compute DDT Sub-Model Calibration Run Input Loads (ug/L)

Source	CHEM1 Orig	Suggested CHEM1 Multiplier	CHEM1 Draft Final	CHEM2 Orig	Suggested CHEM2 Multiplier	CHEM2 Draft Final	CHEM3 Orig	Suggested CHEM3 Multiplier	CHEM3 Draft Final	Comment
NW Br Base	2.28E-04	x 4.0	9.12E-04	0.0	x 4.0	0.0	5.98E-04	x 1.0	5.98E-04	Concentration computed from 6 samples of Gruessner et al. (1998) 1995-96 data
NW Br Storm	1.25E-03	x 4.0	5.00E-03	0.0	x 4.0	0.0	1.54E-04	x 1.0	1.54E-04	Concentration computed from 4 samples of Gruessner et al. (1998) 1995-96 data
NE Br Base	2.33E-04	x 4.0	9.32E-04	5.24E-04	x 4.0	2.10E-03	6.27E-04	x 1.0	6.27E-04	Concentration computed from 6 samples of Gruessner et al. (1998) 1995-96 data
NE Br Storm	1.04E-03	x 4.0	4.16E-03	7.10E-05	x 4.0	2.84E-04	2.54E-04	x 1.0	2.54E-04	Concentration computed from 4 samples of Gruessner et al. (1998) 1995-96 data
SSTrib Base	2.31E-04	x 20.0	4.62E-03	2.62E-04	x 15.0	3.93E-03	6.13E-04	x 20.0	1.23E-02	Estimated to be the averaged NE/NW Branches baseflow (Gruessner et al., 1998)
SS Trib Storm	1.5E-04	x 20.0	3.00E-03	8.85E-04	x 15.0	1.33E-02	1.71E-03	x 20.0	3.42E-02	From available DC MS4 monitoring data, 20 samples with 15 NDs.
CSO	1.5E-04	x 20.0	3.00E-03	8.85E-04	x 15.0	1.33E-02	1.71E-03	x 20.0	3.42E-02	From available DC MS4 monitoring data, 20 samples with 15 NDs.

Table 3-28. WASP Input Parameters for DDT Sub-Model

Process	Parameter	Units	CHEM1	CHEM2	CHEM3	Source
<i>Downstream Boundary Condition:</i>						
	Potomac Boundary Concentration	ug/L	2.30E-05	5.27E-05	3.35E-05	DDE, DDT: Velinsky et al. (1999) DDD: calibration
<i>Adsorption:</i>						
	K _d for fine-grained sediment	L _w /kg _s	80,000	100,401	2,602,545	Mean K _d based on site-specific baseflow data
	K _d for medium-grained sediment	L _w /kg _s	20,000	25,100	650,636	¼ of mean K _d

Table 3-29. Average Annual Load Contributions and Losses by Source for Calibrated DDT Sub-Model

	p,p DDD		p,p DDE		p,p DDT	
	kg	% ²	kg	%	kg	%
Upstream	0.40	66.3	0.09	12.7	0.05	6.4
SS Tribs	0.08	12.8	0.19	27.8	0.51	62.6
LBD	0.07	12.3	0.28	41.5	0.04	4.5
Watts	0.02	3.0	0.05	6.7	0.01	0.8
CSOs	0.03	5.6	0.08	11.3	0.21	25.7
Total Input ¹	0.61	100	0.68	100	0.82	100
Export to Potomac	-0.12	-20.4	-0.15	-22.2	-0.18	-21.6

¹ Total Input is the sum of loads from upstream, SS Tribs, LBD, Watts and CSOs.

² % represents the percentage of total input (sum of all loads).

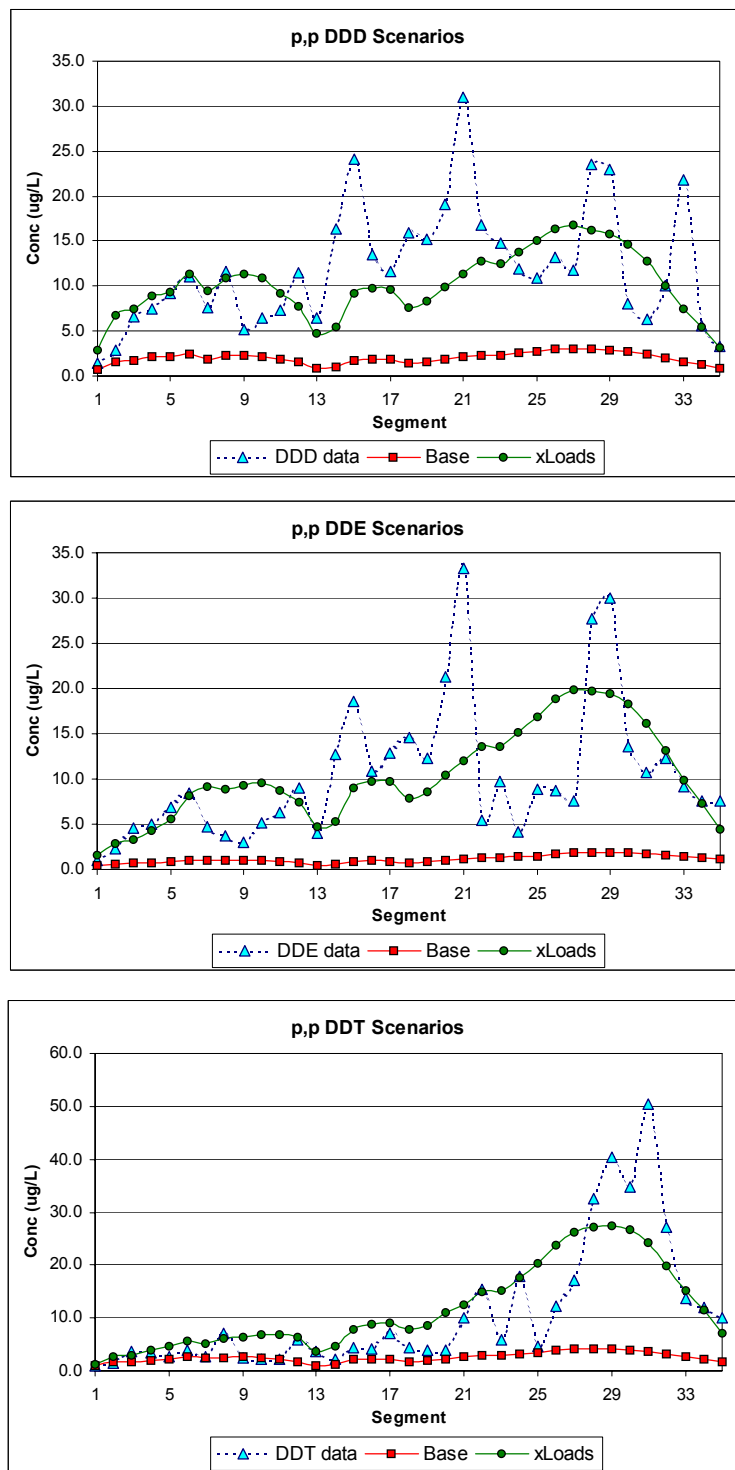


Figure 3-75. DDT Bed Sediment Results: Last day of 6-year run for base scenario (*Base*) and with CSOs and SS Tribs loading increased by 20.0 (*xLoads*)

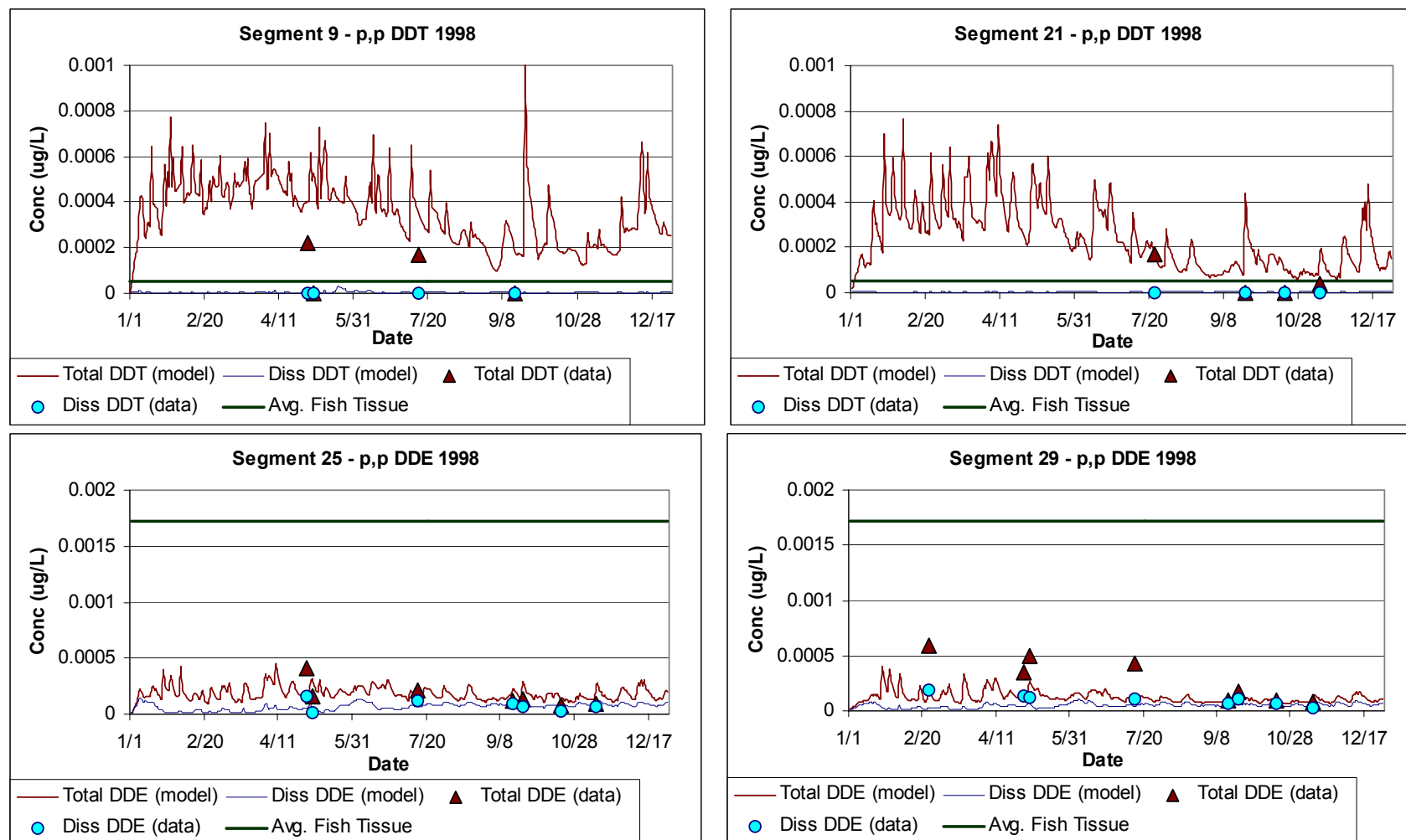


Figure 3-76. Predicted vs. Measured Water Column DDE Concentrations (ug/L) for Base Run Scenario. Estimated Water Column Concentration Based on Fish Tissue Data Analysis also Shown for Comparison

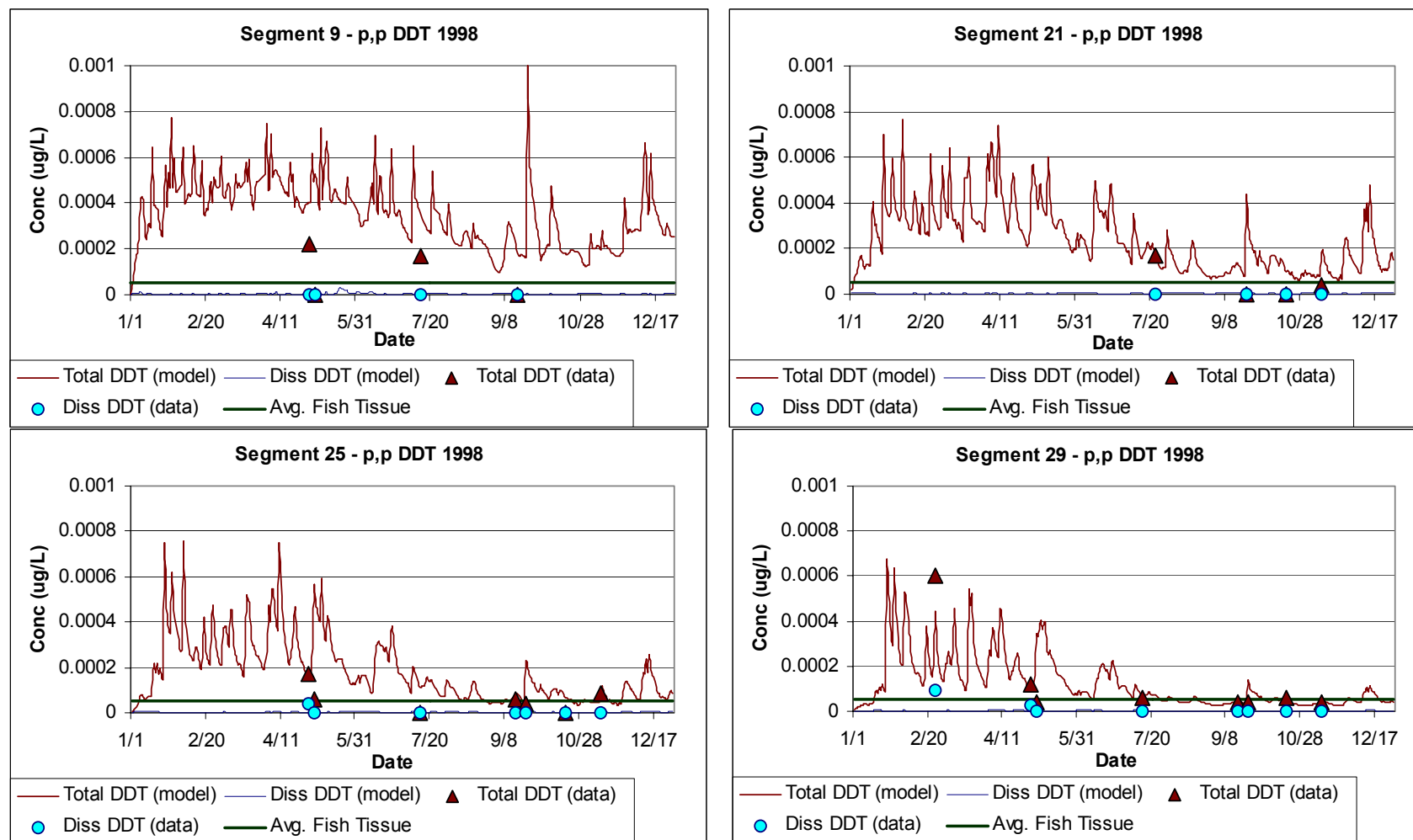


Figure 3-77. Predicted vs. Measured Water Column DDT Concentrations (ug/L) for Base Run Scenario. Estimated Water Column Concentration Based on Fish Tissue Data Analysis also Shown for Comparison

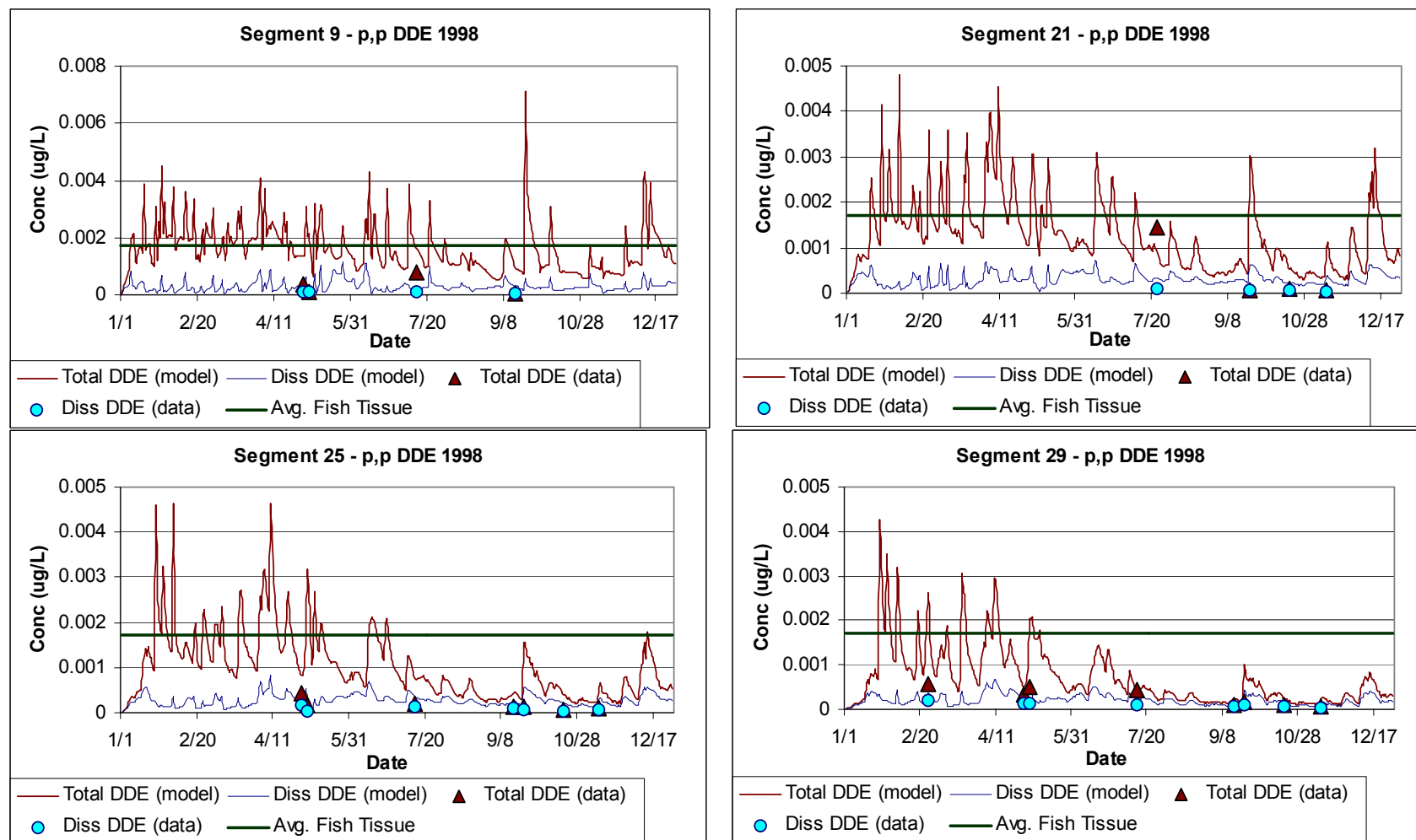


Figure 3-78. Predicted vs. Measured Water Column DDE Concentrations (ug/L) with Upstream Loading Increased by a Factor of 4 and Downstream Loading Increased by a Factor of 15 (note the change in scale for each segment). Estimated Water Column Concentration Based on Fish Tissue Data Analysis also Shown for Comparison

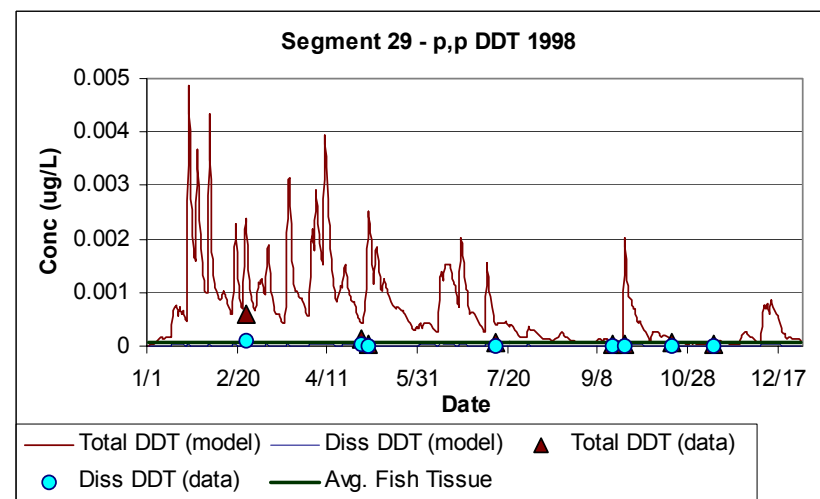
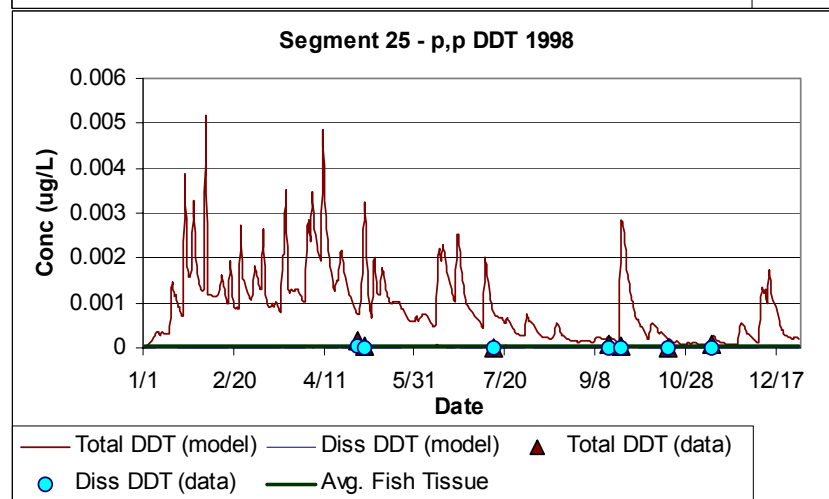
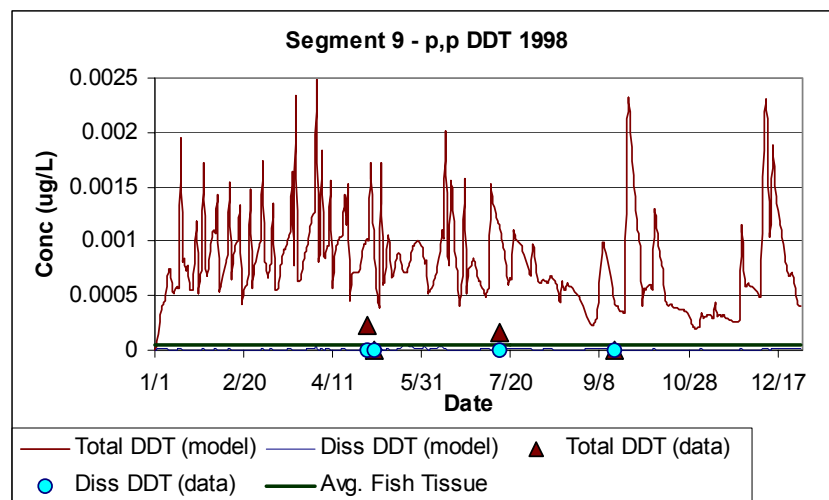
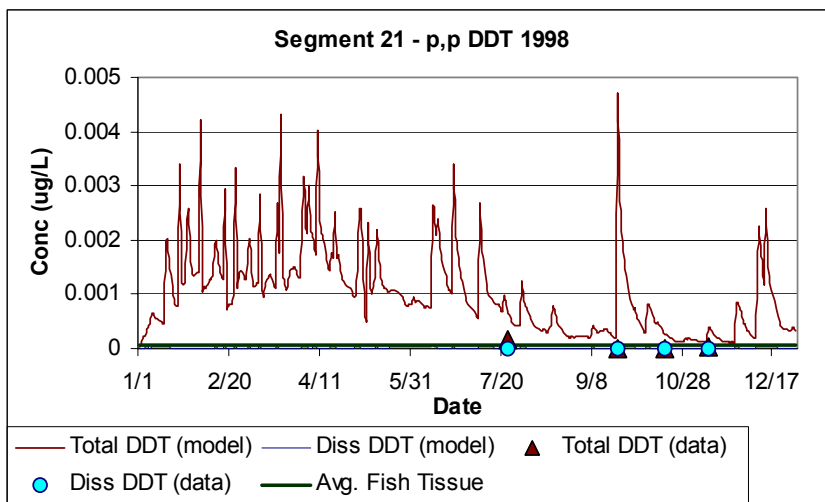


Figure 3-79. Predicted vs. Measured Water Column DDT Concentrations (ug/L) with CSOs and SS Tribs Loading Increased by 20.0 (note the change in scale for each segment). Estimated Water Column Concentration Based on Fish Tissue Data Analysis also Shown for Comparison



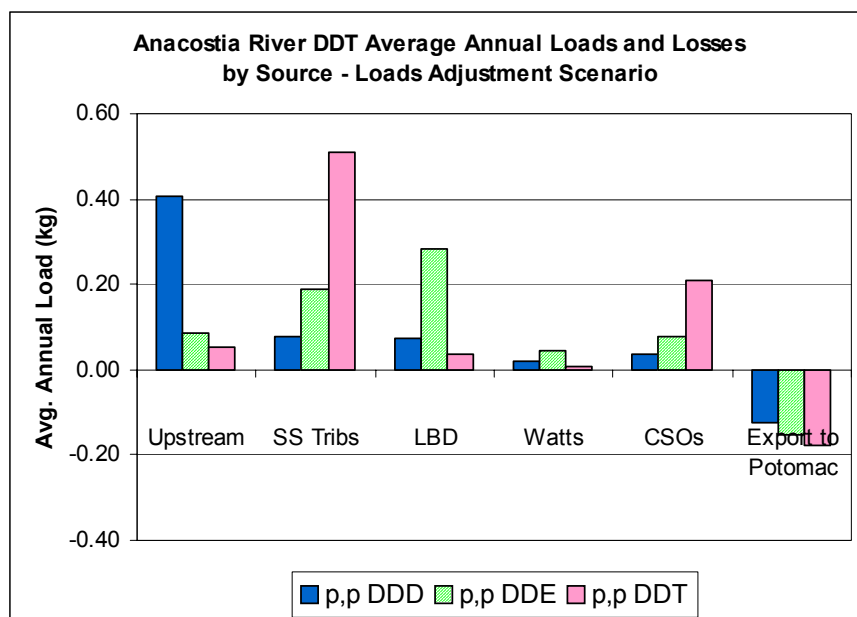


Figure 3-80. Summary of Average Annual Loads and Losses for the Calibrated DDT Sub-Model

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